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XXVII. *On the Strength of Tungsten Single Crystals and its Variation with Temperature.* *By* The Research Staff of the General Electric Co., Ltd.* (*Work conducted by* F. S. GOUCHER.)

[Plates VI.–VIII.]

Summary.

BY heating drawn tungsten wires to a high temperature, large crystals are developed with random orientation of crystal axes, many of which occupy locally the complete volume of the wire. If these wires are subjected to a suitable tensile stress, some of these large crystals will deform by a process of slip; and one will eventually fracture. The orientation of the crystal axis in this crystal is such that two sets of slip planes are symmetrically inclined to the direction of stress, and the crystal fractures in the form of a wedge symmetrical to the stress. This affords a very simple means of studying the deformation of single crystals under conditions involving a minimum distortion of the crystal lattice.

Measurements are made on the strength of such crystals in wires of various diameters and at temperatures varying from 700° K. to the melting-point. It was found that the time required for fracture —which may be regarded as an inverse measure of the mean rate of deformation—is approximately an exponential function of the load and the temperature; that for a given rate of deformation the load is proportional to the cross-sectional area; and—apart from transition temperatures—is a linear function of the temperature.

* Communicated by the Director.

Discontinuities occur in the load-temperature curves at temperatures approximately 850°, 1600°, and 2600° K. Variations in other physical properties are found to occur at the same temperatures, which leads to the view that these changes represent "transformation points" of a new type. Some new measurements on the thermal expansion of tungsten are recorded.

(1) *Introduction.*

THE deformation of single metallic crystals under stress has been studied by G. I. Taylor and C. F. Elam * working with aluminium, and by Polanyi and his collaborators working with zinc † and tin ‡. It has been established for all these metals that deformation takes place by slip on certain crystal planes characteristic of the metal, and that this usually results in a re-orientation of the crystal axis. In the case of aluminium it was shown that the crystal tended to assume an orientation such that two sets of slip planes were symmetrical with the direction of stress ; and it appeared probable that there would be an equal amount of slipping on these two sets of planes near the point of fracture if this condition were completely realized : in this case the fracture would be a wedge symmetrical to the stress.

But no systematic study appears to have been undertaken on the strength of these crystals, taking into account the relation between the rate of deformation on the one hand, and the load, temperature, and orientation of the crystal planes on the other. Such a study would be very difficult if ingots composed of a single crystal were used ; for in such ingots there is no constant relation between the direction of the crystal axis—before deformation—and the external form of the ingot ; which no doubt accounts for the wide variation of tensile strength observed in such ingots §. This difficulty might be overcome by the use of long fine wires made up of many crystals oriented in all directions, of which a considerable number occupy locally the complete volume of the wire. In such a wire chance would insure that at least one of them would be oriented relative to the axis of the wire very nearly in the direction most favourable to slip under stress applied along the wire. If the wire is stretched, slip should occur most easily in that crystal which has the most

* G. I. Taylor and C. F. Elam, Roy. Soc. Proc. A, vol. cii. p. 643 (1923).

† Mark, Polanyi, and Schmid, *Zeit. f. Phys.* xii. (1922).

‡ Mark and Polanyi, *Zeit. f. Phys.* xviii. pp. 75–96 (1923).

§ H. C. H. Carpenter and C. F. Elam, Roy. Soc. Proc. A, vol. c. p. 329 (1922).

favourable orientation; and if the wire is broken, the fracture should occur by a division of this crystal into two wedges symmetrical to the direction of stress, with re-orientation of the crystal axis. Our experiments show that these conditions can be realized in tungsten wires which have been given a suitable heat treatment, if wires 10 cm. long and less than 0·20 mm. diameter are used. Further, tungsten is a suitable metal for such investigations, because it can be obtained exceptionally pure, and the conditions of crystal growth can be so regulated that the crystals are very uniform.

(2) *Material Employed.*

The tungsten wires employed in the investigation were made by the usual process of reducing the oxide in hydrogen, and pressing, "forming," swaging, and drawing the resulting metal. The oxide employed was prepared with all possible precautions for purity; most of the impurities left were removed during "forming," that is to say, heating the pressed bar to a temperature in the neighbourhood of its melting-point. Ordinarily a forming temperature just under 3000°K. is employed, but in the case of most of the wires studied a temperature somewhat above 3000° K. was used. As a result of this treatment, and of that involved in growing comparatively large crystals in the wire, the residual impurity was reduced below 0·01 per cent.

The drawn wire is, of course, fibrous; but if this wire is heated for a few minutes to a temperature about 3000° K., "Recrystallization" takes place, with a random orientation of crystal axes, and rapid crystal growth occurs with the result that many of the crystals fill the whole cross-section of the wire. This treatment was applied to all wires used in these experiments before the measurements were made, and no material was accepted which did not show a reasonably symmetrical wedge-shaped fracture, characteristic of single crystals in the most favourable orientation.

Photographs 1, 2, 3 (Pl. VI.) show such fractures. 1 is a perspective view of a wedge, the outline of the crystals being revealed by etching; 2, 3 show views of another wedge in perpendicular directions. The partially-formed wedge should be noted; it is markedly asymmetrical, as compared with the almost perfect symmetry of the wedge at which fracture has occurred; but in both wedges, the reduction of area has occurred in one plane only. Figs. 4, 5, and 6 (Pl. VII.) show sections through wires, etched to show the crystal structure. Fig. 4 shows a wedge fracture in a single crystal. Fig. 5

shows a partially-formed wedge in one of the smaller wires, the deformed part being again a single crystal; the neighbouring crystals are not deformed. Fig. 6 is a section of the thickest wire used (0·195 mm. diameter); it shows that even in this wire, crystals occupying the full cross-section of the wire are obtained, and that deformation—asymmetrical in this case—is confined within the limits of such a large crystal. These photographs provide sufficient evidence that the fractures studied are, like those of aluminium, true single crystal fractures; and that approximately symmetrical wedges are formed at fracture.

Sykes * has previously observed similar wedge-shaped fractures in molybdenum wires, and Jeffries and Archer †, before Taylor and Elam's work was published, suggested that such wedges might have been caused by slip on conjugate planes inclined at 45° to the axis of the wire.

(3) *Deformation of Tungsten Crystals.*

X-ray analysis was used to determine the nature of the deformation produced in the fractured crystals. A spectrometer of the photographic type was employed, using Cu Kα-radiation; the constants of the spectrometer were determined by means of a crystal of rock-salt. Since the crystal structure of tungsten is known ‡, the reflecting planes could be identified by the position of the reflexions on the photograph.

Figs. 7–11 (Pl. VIII.) show such photographs. Fig. 7 was taken with a thoroughly annealed fine tungsten wire—composed of many small crystals oriented at random—rotating at the spectrometer axis parallel with the X-ray beam. The wire did not extend fully across the beam, and consequently lines appear only in the upper half of the photographs. The lines shown are those corresponding to the (110), (100), and (112) planes.

Reflexions from individual crystals, in particular those forming wedges, were obtained by mounting the wires in hard glass and cutting sections through them in such a way that the surface of the crystal to be examined alone was exposed. The surfaces were polished and etched, and the reflecting planes most nearly inclined to these sections gave intense lines, which were as sharp as those obtained from uncut crystal. Fig. 8 shows the reflexion obtained from a section perpendicular to the axis of the wire through the crystal

* W. P. Sykes, Am. Inst. Mining Eng. Trans. Feb. 1921.

† Z. Jeffries and R. S. Archer, Chem. & Met. Eng. xxvii. p. 751 (1922).

‡ P. Debye, *Phys. Zeit.* xviii. p. 483 (1917).

forming a wedge; many such photographs, taken from sections cut through different positions of wedges, and from wedges formed at different temperatures, establish the fact that the crystal forming the wedge has its (110) plane perpendicular to the axis of the wire within about 10° in all cases. In fig. 9 the reflexion was from a section parallel to the edge of the wedge and inclined to the axis of the wire; the (112) plane is indicated. Fig. 10 shows a reflexion from a section inclined to the axis of the wire, but perpendicular to the plane containing the wedge edge and the wire axis; it shows a (100) reflexion. These reflexions are consistent with a single crystal formation. It is to be noted, however, that the lines in figs. 9 and 10 are not sharp, but are drawn out in a direction parallel to the spectrometer slit, which indicates a slight curvature in the crystal planes.

This analysis shows, therefore, that deformation has not been accompanied by any break-up of the crystal or any marked re-orientation of the crystal axis. It must therefore have occurred as the result of slip along definite crystal planes, and the planes of slip must be of the form $(11n)$. The (112) planes are the most probable, having the widest spacing and the densest packing of atoms; the full evidence that they are indeed the slip planes will be given in a later paper. It is remarkable that the (112) planes rather than the (100) are the planes of slip, for the (100) were found to be the cleavage planes.

It is of interest to note that the particular orientation of the crystal axis with respect to the wire axis in the case of the crystals which fracture is that found by Burger * to predominate in drawn tungsten wire, although the wire was drawn from a crystal aggregate with random orientation of crystal axes. Our experiments show that with this orientation the crystal is stable, and they yield the additional information that under these conditions the crystal offers minimum resistance to symmetrical extension by a process of slip.

The measurements about to be described on the laws of flow of these crystals may therefore be considered as applying to that condition of the crystal which most frequently occurs in the crystal aggregate when deformed under drawing stresses.

(4) *The Mechanism of Deformation.*

We reserve fuller discussion of the formation of the wedge to a later paper, but certain conclusions with regard to this are of importance in connexion with the interpretation of

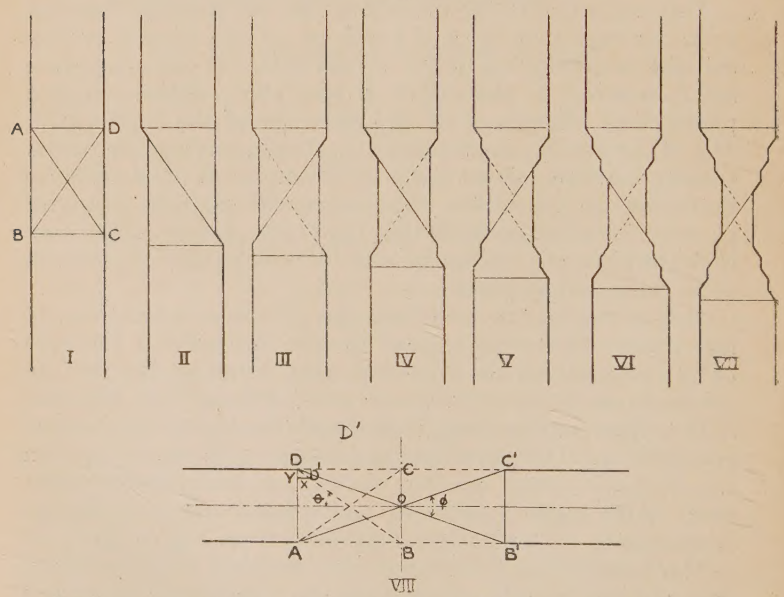
* H. C. Burger, *Phys. Zeit.* xxiii. p. 141 (1922).

the measurements to be described. These have to do with the time required for fracture and the extension of the crystal during fracture.

The manner of formation of these symmetrical wedges must be that suggested by Jeffries and Archer, except that in this case the slip planes are not inclined at an angle of 45° to the direction of stress, as he supposed, but at the more oblique angle of 35° 15′. They assumed a succession of slips on alternate conjugate slip planes, which results in an extension of the crystal and at the same time a reduction of the diameter in a plane perpendicular to the two sets of slip planes. The reasons for this alteration of slip need not concern us here.

Such a process is illustrated by the diagrams I–VII (fig. 1),

Fig. 1.



VIII

which represent successive stages of deformation of a crystal in a test curve. These diagrams are similar to those given by Jeffries and Archer. ABCD (No. I) represents a section of a crystal cut parallel to the wire axis, AC and DB being the directions of the two sets of slip planes. Nos. II–VII show a succession of slips which result in a progressive extension of the crystal and at the same time a progressive reduction of the diameter in the plane of the section. If the slips are small in comparison with the dimensions of the crystal, and if there is on the average just as much slipping

on one set of planes as on the other, a completely symmetrical fracture may be produced. Without making any assumptions as to the extent of slipping on any one plane or as to the numbers of slips required for fracture, it follows that the extension of the crystal is a function of the angle made by the slip planes with the direction of the wire axis and the diameter of the crystal before deformation.

Consider the diagram No. VIII. Let ABCD represent the crystal before deformation and DOA and C'OB' two parts of the divided crystal just after fracture. Let DB and AC represent the directions of the slip planes which make an angle θ with the direction of the wire axis. Then any small slip DD' along DB may be represented as an extension x in the direction of the wire axis, and as reduction of diameter y perpendicular to the wire axis where

$$y = x \tan \theta.$$

If we consider the fractured crystal as having been produced by the summation of a larger number of such slips parallel to DB or parallel to AC, then the total extension BB' will be given by

$$BB' = \Sigma x = \Sigma y \cot \theta.$$

But Σy is equal to AD when fracture occurs, so that

$$BB' = AD \cot \theta.$$

For the value $\theta = 35° 15'$,

$$BB' = 1{\cdot}41 \text{ AD}.$$

It may be pointed out that the angle ϕ of the symmetrical wedge formed by such an extension will be given by

$$\phi = 2 \tan^{-1} (\tfrac{1}{2} \tan \theta),$$

which, if $\theta = 35° 15'$,

gives $\phi = 38° 56'$.

Many crystal wedges formed by fracture of the test wires had angles agreeing with this value within one or two degrees. Such a wedge is that shown in photo No. 4 (Pl. VII.).

A large number of wedges had angles larger than this value, but the results of experiments to be described in a later paper showed that the slip planes were the same as in the case of the narrow wedges, though the relative amount of slipping on the two sets of slip planes was not the same, owing to a slight asymmetry in the inclination of the crystal axis with respect to the direction of stress. This slight asymmetry would not, however, appreciably effect the total amount of extension required for fracture.

Assuming that the mechanism of fracture is substantially that described, it is clear that the time required for fracture serves as a measure of the mean rate of slip or extension within the crystal which fractures ; and that in studying the conditions for fracture the time for which the load is applied is quite as important as the load or the temperature.

Doubtless, owing to the progressive reduction in area of the slip planes, the rate of extension will increase rapidly near the point of fracture ; and if distortion of the slip planes occurs the rate of extension will be altered. But it may be safely assumed, however, that crystals of equal diameter which deform into similar wedges on fracture will deform at the same mean rate if the time required for fracture is the same.

(5) *Apparatus.*

In studying the strength of these crystals, a measured tension was applied to the wire electrically heated in vacuo, and the time for fracture noted. The temperature was determined by using the well-established relations of Langmuir * between current and temperature.

The apparatus consisted of a tungsten and steel buoy floated in mercury, and attached to the lower end of the wire, the upper end of which was fixed. The amount of tension could be regulated by depressing the mercury level below the floating-point of the buoy by means of a mercury column controlled from outside the vacuum ; the control included a slow-motion device.

Fig. 2 gives a diagrammatic view of the experimental arrangement. The wire W is attached at its upper end by means of a clamp C_1 to a removable stopper J, which can be sealed with mercury into the containing vessel. At its lower end the wire is attached by means of a clamp C_2 to the tungsten and steel buoy $R_1 S R_2 T$, which is constructed as shown. T is a heavy mass of tungsten ; S is a steel cylinder ; R_1 and R_2 are supporting rods of small diameter which serve to space the steel and tungsten so that the centre of gravity of the system is low. They also pass freely through two holes in the guide-piece G, which is necessary to keep the buoy from touching the sides of the glass vessel. G is so constructed that it lightly grips the sides of the glass vessel when the wire, with buoy attached, is lowered into position, and it may be removed with the buoy. B is a section of rubber tube fastened to the glass vessel so as to act as a buffer for the falling buoy when the wire breaks.

* I. Langmuir, Phys. Rev. vii. p. 302 (1916).

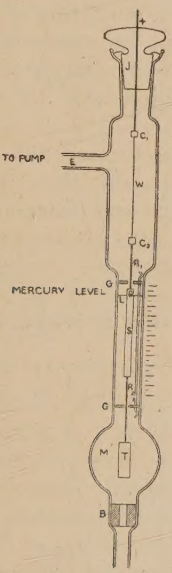
If the friction is negligible, the tension T will be given by

$$T = \frac{\pi D^2 \rho h}{4},$$

where D is the diameter of S ; ρ the density of mercury; and h the displacement of the mercury level from the floating-point.

Calibration of the buoy could be carried out by attaching the upper end to a beam balance in the open air and varying the mercury level, the whole operation being carried out with the buoy in position in the glass containing vessel.

Fig. 2.



Such a calibration showed that the friction forces could be neglected and that the calibrated value could be used. A wide range of tensions varying from a fraction of a gram to several hundred times that value could be covered by the use of a few buoys of different sizes.

The wire was heated electrically through the lead to C_2 sealed into the glass stopper J, and by means of the mercury. The current was measured on a standard Weston Ammeter.

The pumping system was such that a pressure less than 0·001 mm. Hg. could be attained in a few minutes, and liquid air was used near the containing vessel. Under these conditions the current temperature relations accurately applied.

(6) *Method of Measurement.*

As it was necessary to give the wires a preliminary heat treatment in order to develop a suitable crystal structure before applying the tension, the procedure adopted was as follows:—

(1) The wire in the hard-drawn state was clamped between C_1 and C_2 outside the containing vessel, and the whole was lowered into position in the vessel and J sealed with mercury; the total weight of the buoy is easily sustained by the wire in the drawn state.

(2) The vessel was exhausted and the mercury level brought to the floating-point marked on the buoy, so that the wire was put into a condition of no tension.

(3) The wire was given its preliminary heat treatment; at the same time it was straightened by means of a very slight tension, which was less than that required to stretch the wire.

(4) The tensile test was carried out by applying the tension to the wire when cold, then heating the wire to the desired temperature and observing the time required for fracture. As the wire always extended during fracture, the level of the mercury was kept a constant distance below the floating-point by depressing the mercury level at a rate equal to that at which the wire extended.

(7) *Experimental Results.*

Measurements were carried out on these test wires under a wide variety of conditions of wire diameter, temperature, load, and time required for fracture. It was found that symmetrical wedge-shaped fractures of the same type occurred at all temperatures between 700° K. and the melting-point; and that the time required for fracture under given conditions of load and temperature could be varied at will from a few seconds up to an indefinite time. As the observations became more variable as the time was increased, ten minutes was adopted as the upper limit in the case of the measurements described. In every case the time (t) required for a load (L) to break a wire of cross-sectional area (σ) at a temperature (T) was observed directly. But by a suitable combination of the observations the following relations which are specially important can be deduced:—

(1) L, t variable; σ, T constant.
(2) L, σ ,, t, T ,,
(3) t, T ,, L, σ ,,
(4) L, T ,, σ, t ,,

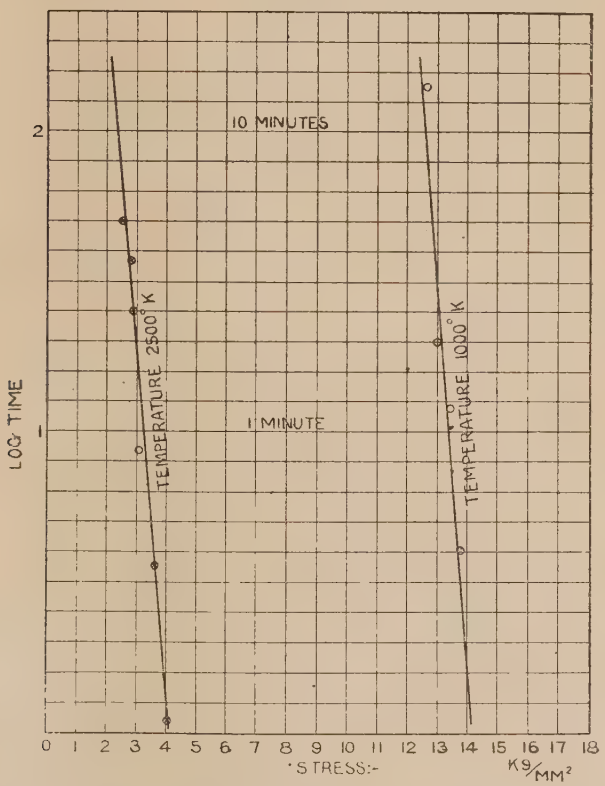
As the relations deduced are derived from the same observations, they are inevitably consistent with each other.

(8) *The Relation between Time and Load.*

Though the time to fracture varies very rapidly with load, measurements could be obtained which clearly showed the law governing this change for a range of time varying from a few seconds up to ten minutes or more.

Typical time-load curves are shown in fig. 3, in which the

Fig. 3.

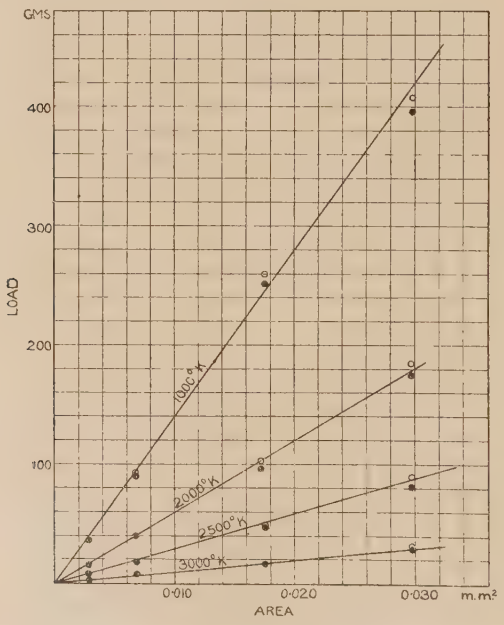


logarithm of the time in minutes is plotted against L/σ expressed in kg./mm.^{2} Two curves are shown—one for a temperature of 2500° K., and one for a temperature 1000° K. The test-wires were of a diameter 0·093 mm., the preliminary heat treatment being 3100° K. for two and a half minutes. Similar curves were obtained for wires of other diameters, the slope being approximately the same in all cases.

(9) *The Relation between Load and Cross-sectional Area of the Test-wire.*

By taking a sufficient number of time-load curves for wires of different diameters, at the same temperature, the load required to fracture such wires could be obtained as a function of the cross-sectional area of the test-wire for any arbitrary value of time. If equal mean rates of deformation are required, the times must be chosen as proportional to the wire diameter; but as the time to fracture varies rapidly with the load, a comparison on the basis of equal times would introduce relatively small errors.

Fig. 4.

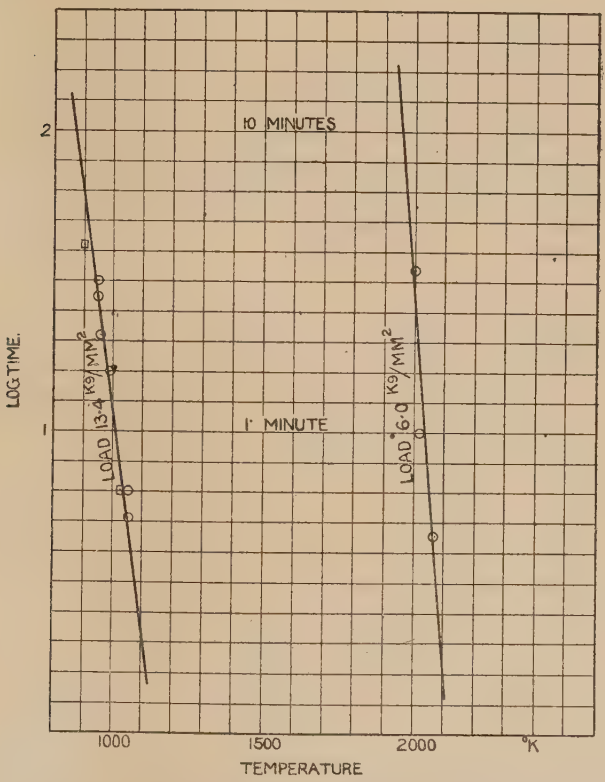


Curves (fig. 4)—points marked—summarize the measurements made in this way; the load in grammes required to fracture the wire is plotted against the cross-sectional area of the wire in mm.^{2} The black circles represent values of load for time chosen proportional to the diameter, that for the smallest wire being one minute; the open circles represent values for equal times, viz. one minute. The wires varied in cross-sectional area from 0·0028 mm.^{2} for wires 0·06 mm. in diameter to 0·0297 mm.^{2} for wires 0·195 mm. in diameter. The preliminary heat treatments varied from 2900° K. for 1 minute in the case of the smallest wire to 3100° K. for 2½ minutes for the largest. The observations

were made at four different temperatures, viz. 1000°, 2000°, 2500°, and 5000° K.

It is clear that the variations in the strength of the crystals from wire to wire are greater than the differences introduced by this change in the ratio of times. We may consider, however, that within the limits of experimental error the load required to fracture these crystals at a constant rate of

Fig. 5.



deformation and at the same temperature is proportional to the cross-sectional area of the crystal before deformation, over a wide range of the variables.

(10) *The Relation between Time and Temperature.*

The curves of fig. 5 show the relation between temperature and the time required for a given load to fracture the wire; the logarithm of the time is plotted against the temperature. Curves for two different loads are shown, viz. 13·4 kg./mm.^{2} and 6·0 kg./mm.^{2}; the test-wires were 0·093 mm. in diameter, and

the preliminary heat treatment was 3100° K. for 1½ minutes The experiments are not capable of great accuracy because the time varies so rapidly with the temperature; but they are sufficient to show that the observations tend to lie on straight lines. Consecutive portions of the test-wires naturally gave the most consistent results. Very large numbers of curves of this same type were obtained with all wires and for all values of load which fractured these wires in measurable times at temperatures ranging from 700° C. to very near the melting-point.

Some observations were also made by another method. The squares plotted on the curve for the load 13·4 kg./mm.^{2} were obtained by heating the test-wires in an electric furnace—within the vacuum,—the temperature being obtained by means of a calibrated thermo-couple of nickel-nichrome. This was done as a check on the method of heating. The results of the two methods agree within the limits of experimental error.

(11) *Relation between Load and Temperature.*

The consistency of the observations relating to time required for fracture and temperature makes it possible to determine the temperature for a given time and for a given load to within 50° on our temperature scale.

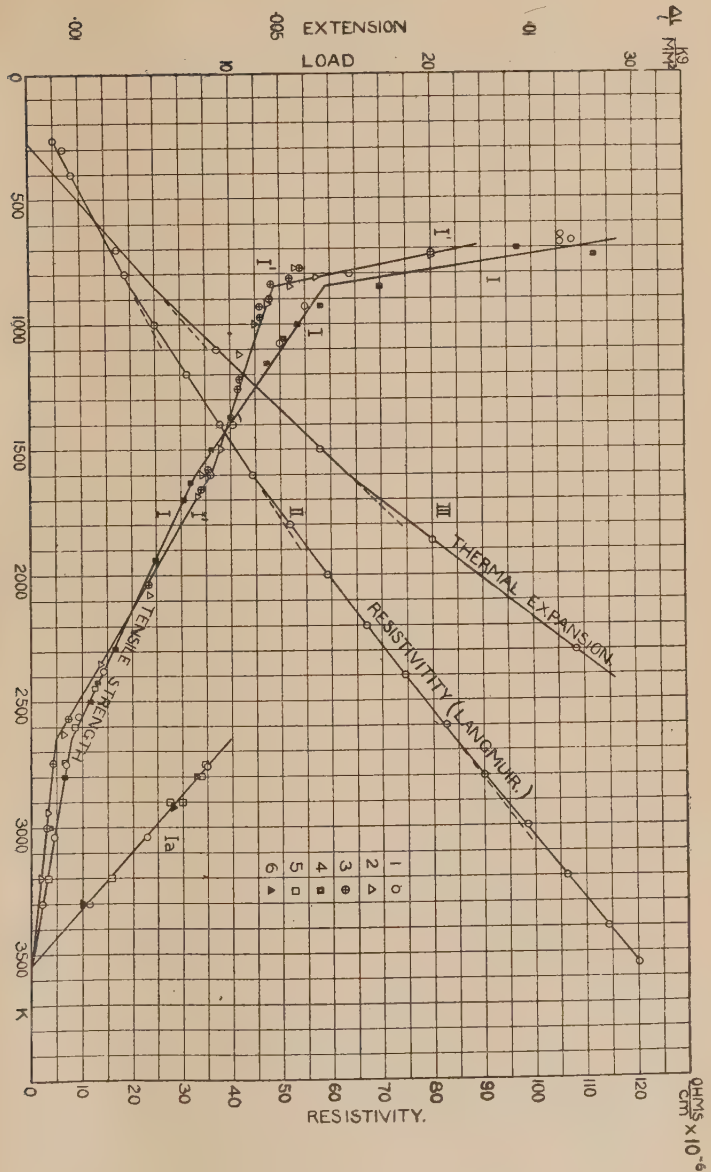
By making a sufficient number of observations relating time and temperature for a given load, so that the temperature corresponding to the one minute value of time could be estimated, the relation between load and temperature was obtained at various temperatures from 700° K. to within a few hundred degrees of the melting-point for a variety of wires of different diameters.

Curves I, I^1, and 1*a* (fig. 6) summarize the results of such measurements. The load in kg./mm.^{2} is plotted against absolute temperature.

The wires used were of different diameters, and were drawn from ingots formed at two different temperatures. The following table gives the key to the observations as plotted in the curves (fig. 6) :—

Wire number.	Diameter mm.	Forming temperature.	Preliminary heat treatment.
1	0·06	above 3000°	2900° for 1 minute.
2	0·05	,, ,,	,, ,, ,,
3	0·06	below 3000°	,, ,, ,,
4	0·093	above 3000°	3100° for 1½ ,,
5	0·195	,, ,,	,, ,, 2½ ,,
6	0·10	,, ,,	2900° ,, 2 ,,

Fig. 6.


EXTENSION
LOAD
KG/MM²
TEMPERATURE
K
RESISTIVITY.
OHMS x 10⁻⁶ CM
TENSILE STRENGTH
THERMAL EXPANSION
RESISTIVITY (LANGMUIR.)
I
I'
II
III
Ia
1 ○
2 △
3 ⊕
4 ■
5 □
6 ▲

Curve I *a* is merely the portion of Curve I above 2700° K. plotted on a magnified scale. Most of the fractures obtained below 800° were probably intercrystalline; a symmetrical wedge was not formed at the fractured end. In this case, however, the crystal was stronger than the crystal boundaries; the observations thus have some significance from the point of view of strength, so some of these are plotted. The crossed circle at 700° K. represents observations made with wires which did form wedges on fracture.

The most remarkable feature of these results is the presence of sharp changes in the load-temperature curves which indicate definite discontinuities. These discontinuities, which are characteristic of each of the wires used, occur at temperatures between 800°–900° K., at about 1600° K., and again at 2600°–2700° K. The observations appear to lie on straight lines between these regions of sharp changes, and for this reason these lines have been drawn through the observed points to intersect at these transition temperatures. It is noteworthy that the straight line above 2700° K.—plotted on the magnified scale in I *a*—appears to cut the temperature axis at a temperature very close to the melting-point, given by Langmuir as about 3570° K.*

But the observations are not wholly consistent; they divide themselves into two distinct groups, which differ particularly in the slopes of the curves on either side of the 1600° K. discontinuity. The division cannot be due to differences of purity which might arise from differences in forming temperature; for though Group II includes the only wire formed at the lower temperature, it includes also the 0·05-mm. wire, which is of the same material as those in Group I and merely drawn to a smaller diameter. Neither can the differences be accounted for by the preliminary heat treatment, as the 0·06-mm. wires in Group I were given the same treatment exactly as those in Group I^1.

The wires falling in Group I^1 appear to give the most consistent results and the sharpest discontinuities. It is possible that this is connected with the previous history of the wires, for although every effort was made to give the same mechanical treatment, variation in die steps and temperatures from wire to wire are unavoidable. Such differences may modify the crystal structure in some way which affects the strength. A further study of the physical properties of these wires may throw more light on this point.

* I. Langmuir, Phys. Rev. vii. p. 302 (1916).

(12) *Variation of other Physical Properties with Temperature.*

The discovery of discontinuities in the relation between load and temperature suggest that existing data on the variation of other physical properties with the temperature should be examined to see if they indicate the presence of such discontinuities.

Curve II (fig. 6) shows Langmuir's values for electrical resistivity* plotted against temperature. Clearly the observed points are consistent with discontinuities at the same transition temperatures as those shown by the strength curves, though the changes are too small to locate these temperatures with any accuracy. The circles (Curve III) show some of Worthing's† observed points for thermal expansion plotted on the same temperature scale. These show changes which are certainly consistent with a discontinuity at about 1600° K., but there are not enough observations to show the presence of any discontinuity at lower temperatures. His results point to a change in expansion coefficient somewhere between room temperatures and 1300° K., but he represents the change as gradual.

These results appear to support the existence of these transition temperatures, but it seemed especially desirable to supplement Worthing's measurements on thermal expansion, in particular at low temperatures.

(13) *Thermal Expansion Measurements.*

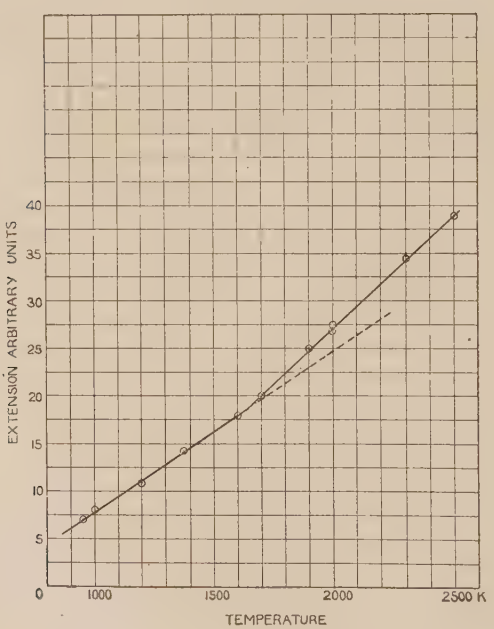
The apparatus used for the tensile strength measurements was well suited for the measurements of expansion of these wires at high temperatures; it was only necessary to observe the extension of the lower end of the wire with a cathetometer when just sufficient tension was applied to the wire to keep it straight, but not enough to give it a permanent extension. The temperatures were measured by the heating current, the error due to the cooling at the ends of the filament being eliminated by measuring the extension for two different lengths of the filament and taking the difference in the extensions at corresponding temperatures.

Fig. 7 shows a typical extension–temperature curve obtained with a wire 12 cm. in length. The extension is plotted in arbitrary units. The observations clearly lie on straight lines, above and below a temperature between 1600° K.

* I. Langmuir, Phys. Rev. vii. p. 154 (1916).
† A. G. Worthing, Phys. Rev. x. p. 638 (1917).

and 1700° K. A similar curve was obtained for a wire 24 cm. in length, and the slope of the difference curve yielded values of the coefficient of expansion which agreed well with Worthing's values, especially above the transition temperature. Observations of this type were made on wires of three different diameters: all agreed in giving a transition temperature of about 1650°, and the coefficients of expansion calculated were 7·34, 7·17, and $7{\cdot}30 \times 10^{-6}$ respectively above the transition temperature and 5·80, 5·30, and $6{\cdot}0 \times 10^{-6}$ below the transition temperature. The mean of the higher value, $7{\cdot}27 \times 10^{-6}$, agreed very well with Worthing's value

Fig. 7.

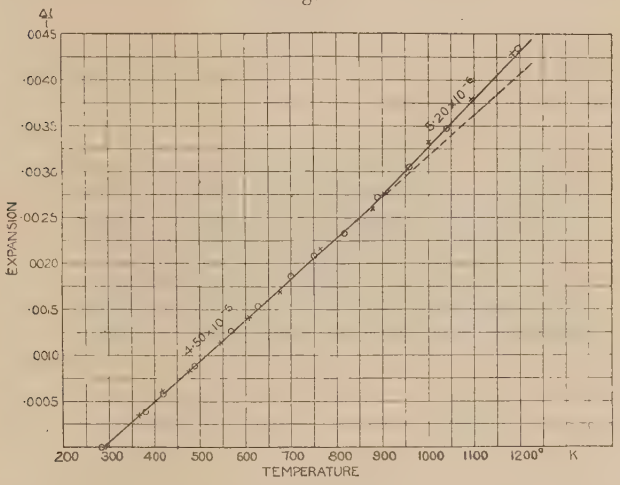


$7{\cdot}26 \times 10^{-6}$ for the temperature 2300° K., that of the lower value $5{\cdot}71 \times 10^{-6}$ being somewhat high as compared with Worthing's value $5{\cdot}19 \times 10^{-6}$ for temperature 1300° K. The higher values were considered much more reliable, as the measured extensions were so much larger, and the wires were no doubt straighter at the higher temperatures. There is no doubt, however, about the sharpness of the discontinuity under these experimental conditions. It is to be noted that

the measurements were made under conditions of slight tension.

In order to investigate the expansion at lower temperatures a different method was employed. The expansion of a tungsten rod 1 mm. in diameter was measured by comparing its expansion with that of silica in an electric furnace, the temperature of which was measured by means of a platinum-rhodium thermo-couple. The first measurements on this tungsten rod did not indicate any sharp discontinuity at the temperature expected, but by annealing it very near its melting-point consistent results were obtained which clearly revealed a discontinuity. The results of these measurements are summarized in curve (fig 8), in which the observed points

Fig. 8.



represent two sets of readings. They clearly show that a sharp discontinuity in the expansion curve exists at about 850° K., which is in good agreement with the transition temperature indicated by the tensile-strength measurements. Here, again, the coefficients of expansion are constant above and below that temperature. The value below 850° K. was $4{\cdot}50 \times 10^{-6}$ as compared with Worthing's value of $4{\cdot}44 \times 10^{-6}$ for room temperatures; above 850° K. the value was $5{\cdot}20 \times 10^{-6}$, which is in excellent agreement with Worthing's value for 1300° K.: it therefore appears most probable that this value holds up to 1600° K. It is to be noted that these measurements were made under conditions which put the specimen under very slight compression.

Fig. 6 (Curve III) summarizes in heavy line the results of the thermal expansion measurements, Worthing's values being represented by the circles. Clearly our measurements are not inconsistent with his, but they go further in that they reveal the constancy of the coefficients apart from these transition temperatures.

The measurements were not carried out above 2600° K. so that no check was obtained on the 2600° K. discontinuity found in the case of the tensile-strength curves.

(14) *Discussion.*

The chief results of our experiments are those which concern, first, the relations between the variables affecting deformation, second, the existence of transition temperatures for the physical properties of tungsten.

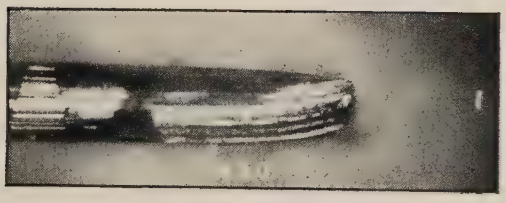
We find that the time of fracture which we regard as an inverse measure of the mean rate of deformation is approximately an exponential function of the load and the temperature. For a given mean rate of deformation the load is proportional to the cross-sectional area and, between transition temperatures, is a linear function of the temperature.

The only experiments on single crystals with which we can compare our own are those of Schönborn *, who also found that the rate of deformation was an exponential function of the load. His absolute values varied from specimen to specimen, doubtless because he did not secure a constant relation of crystal axis to direction of stress. But some of our relations accord well with those found in crystal aggregates, and suggest accordingly that the laws governing the deformation of such an aggregate are intimately connected with those governing the deformations of the individual crystals. Thus it is known that for such aggregates the rate of extension varies very rapidly with load and temperature. Further, Andrade † in his study of the viscous flow of metal aggregates found that, for a constant rate of flow, the load was proportional to the cross-section. Again, the rate of flow in liquid viscosity is approximately an exponential function of the temperature. Lastly, Jeffries and Archer's ‡ results on the variation with temperature of the tensile strength of

* H. Schönborn, *Zeit. f. Phys.* viii. p. 377 (1921).

† E. N. da C. Andrade, Roy. Soc. Proc. A, vol. xc. p. 329 (1914).

‡ Z. Jeffries and R. S. Archer, Chem. & Met. Eng. xxvii. p. 882 (1922).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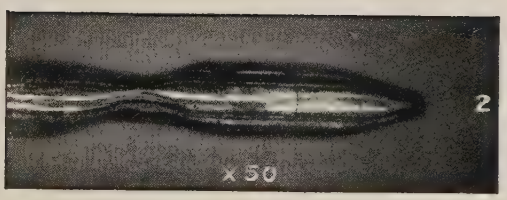
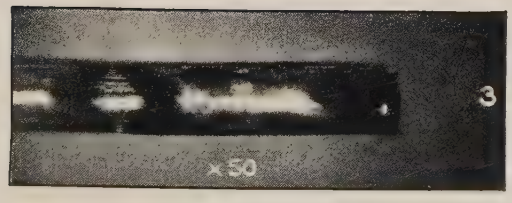

2
×50


3
×50

tungsten agree well with our relation between load for a given rate of deformation and temperature. The multi-crystal wire used by them is many times stronger than our single crystals, but curves of much the same shape are obtained for temperatures ranging from 300° to 1200° K.; in particular they found a change in strength occurring at about 800° K. The comparison cannot be carried to higher temperature because crystal growth affects the results.

The explanation of all these relations doubtless awaits further measurement and the development of the theory of crystal structure. It is to be hoped that this method of measurement, which has yielded such definite results in the case of tungsten, can be applied to other metals.

The significance of the transition temperatures and the nature of the changes which cause the alteration of physical properties at these temperatures are very obscure. Ordinary "transformation points" in metals are usually associated with some re-arrangements of the atoms indicated by a change in the crystal structure of the material. But direct investigation has shown that between room temperature and 2000° K. the crystal structure of tungsten undergoes no change other than that due to mere expansion. Fig. 11 (Pl. VIII.) shows on the same film two X-ray spectra given by the same tungsten wire, one with the wire at room temperature, the other with the wire heated to about 2000° K.; the displacement of the lines at the higher temperatures is just that expected on the ground of expansion.

Perhaps the variation in the nature of the change at the transition temperature, which is indicated by the two curves in fig. 6, may provide the clue. If it can be found why two wires, though showing discontinuities at the same temperature, show different discontinuities, much light will be thrown on the problem. Work is proceeding in this direction; for the time being we would merely conclude that these transition temperatures, though their nature is obscure, are quite as real and definite as the more usual "transformation points."

The Research Laboratories of the G. E. Co. Ltd.,
April 1924.

XXVIII. *The Emission of β- and δ-rays from a Metallic Film, and the Relation to the Quantum Theory of Scattering of X-rays.* *By* Lewis Simons, *D.Sc.* (*Reader in Physics in the University of London*) *.

When X-rays of frequency ν fall upon a metal plate, photo-electrons of all speeds are emitted up to a maximum speed given by v in the equation $\frac{1}{2}mv^2=h\nu$, where m is the mass of the electron and h is Planck's constant. By absorbing these electrons in a layer of air at various pressures, the author succeeded in showing † that minor groups of electrons were also present possessing speeds given by the relation $\frac{1}{2}mv^2=h\nu-p$, where p represents the energy associated with the K, L, M, etc. levels within the atom. The more exact photographic methods employed by de Broglie ‡ and Whiddington § have put the assumptions beyond all doubt.

When the work was resumed in London in 1922, apparatus was set up to measure by the method of a retarding electrostatic field the velocities of the slowest particles emerging. A paper on the subject ‖ and an earlier one by Shearer ¶ are the most recent in which an attempt has been made to discover the laws of emission of the copious stream of δ-rays, which possess an energy of comparatively few volts and which always accompany the emission of the above true photo-electrons. The general conclusions in these two papers were that the δ-rays are many times more numerous than the rapid photo-electrons, and that they are probably produced by collision of the rapid photo-electrons with surrounding atoms. The curves clearly indicate that they form a group quite distinct from the true photo-electrons. The δ-rays of the foregoing work had been produced by the heterogeneous beam from the tungsten anticathode of a Coolidge tube; but by working with a Wilson's tilted electroscope at great sensitiveness, the author has now succeeded in measuring the very feeble photo-electric currents

* Communicated by the Author.

† Phil. Trans. Roy. Soc. S. Africa, viii. 1, p. 73 (1919); Phil. Mag. xli. p. 120 (1921).

‡ *Comptes Rendus*, clxxii. pp. 274, 527, 764, 806 (1921); *Journal de Physique*, p. 265 (1921). See also Report of Solvay Congress, 1921.

§ Phil. Mag. xliii. p. 1116 (1922).

‖ Simons, Phil. Mag. xlvi. p. 473 (1923).

¶ Phil. Mag. xliv. p. 806 (1922).

and the velocities of the δ-electrons emerging from a thin gold film in a vacuum upon which the comparatively homogeneous fluorescent X-radiation from secondary radiators is allowed to fall.

In the meantime an interesting quantum theory of the scattering of X-rays has been worked out by Compton *, in which he shows that if X-rays of wave-length λ_0 fall on a scatterer, then there is an increase in wave-length due to scattering such that

$$\lambda_\theta = \lambda_0 + (2h/mc)\sin^2\theta/2,$$

c being the velocity of light and θ the angle between the incident ray and the direction in which the same scattered ray is observed. This theory is apparently confirmed by Compton's own experiments and by others quoted in the papers, whilst still more recently de Broglie † has obtained photographic proof of the accuracy of the ideas.

Whilst plotting on the same graph—(*a*) the intensity of the true photo-electron emission, as above, against wave-length of the exciting X-rays, and (*b*) the intensity of the concomitant δ-ray emission against the same wave-length,—it was noticed that, after suitable adjustment of ordinates, the curves could be made to coincide with each other if it could also be assumed that the X-rays responsible for the δ-rays were in each case longer than the X-rays responsible for the true photo-electrons by 0·040 Å.U. This is precisely the value given by Compton's formula, where, in the experimental arrangements described below, the angle of scattering ranged over from 180° to 90°. It is therefore suggested that not only does the present experiment add confirmation to this theory of scattering, but that it would now appear that the true rapid photo-electrons are associated with the emission of the fluorescent X-rays or the unmodified scattered rays, whilst the δ-rays are associated with the modified scattered rays.

Apparatus and Experimental Method.

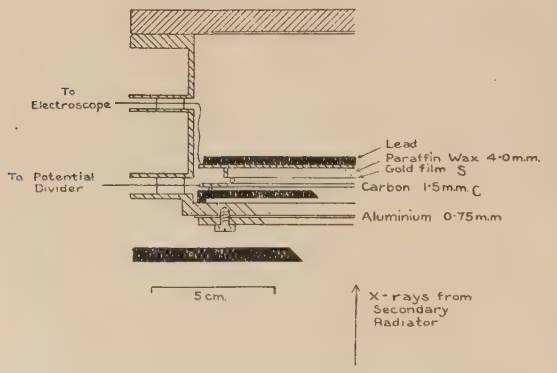
The primary source of radiation was a Coolidge tungsten anticathode radiator pattern X-ray tube worked with a transformer. No variation whatever during working was allowed in this over the whole period of the experiments, lasting some

* Phys. Rev. xxi. pp. 483–502 (May 1923); Phil. Mag. xlvi. pp. 897–911 (Nov. 1923).

† Guthrie Lecture, Physical Society of London, 1924.

months. The heating current remained constant and the tube was always worked with 3 milliamperes passing through it, equal rests being allowed between the readings. A time-factor, not a standardizing electroscope, gave the quantity of X-rays, as it was realized that these experiments deal with the fundamental processes of ionization, and therefore no method employing ionization ought to be used as a standard. The heterogeneous beam fell upon a thick secondary radiator, and the secondary fluorescent beam, limited by suitable stops, passed into the experimental chamber, half of which is shown in fig. 1. It is doubtful whether the crystal reflexion method would have any great advantage over this method, for the radiators are readily interchangeable, and if they are thick they give a fair sample

Fig. 1.



of the incident rays upon them; moreover, a large surface can be exposed to the secondary rays. The angle between the primary heterogeneous beam and the fluorescent secondary radiation was 90°. This secondary beam now fell normally on to an extremely thin film of gold laid down electrolytically on a plate of paraffin-wax 0·4 cm. thick, passing first through the aluminium bottom of the experimental vessel 0·75 mm. thick and a pure carbon plate 1·5 mm. thick. The lid of the vessel was sealed on with resin cerate for ease of removal, and the vessel was exhausted by a mercury-vapour pump. The mean pressure maintained during the experiments was 0·035 mm. of mercury, the pressure being measured by means of a Pirani pressure gauge. The factors deciding this pressure were the ease with which

it could be established and maintained, and the independence of the electrometer readings on small fluctuations about this mean pressure. The screen S, raised on sulphur insulators about 2 mm. from the carbon plate C, was connected by as short a wire as possible to the electrometer, which therefore registered a positive charging. A thick sheet of lead, coated with lampblack, was laid upon the top of the screen, in order to ensure that the positive charging was due only to those electrons emerging from the gold downwards.

The tilted electroscope and the method of using it as a null instrument have been described in a previous paper *. The method ensures that the electrostatic field either retarding or accelerating the electrons remains constant and measurable, which is an obvious advantage when the fall of potential is of the order of a volt or less. The sensitiveness of the electroscope was of the order 0·007 volt per eyepiece scale division, and one-tenth of a scale division could be estimated. The capacity of the electrostatic system was about 40 cm. The time of run of the X-ray tube was varied only from 2 to 4 minutes, it being felt that larger variations than this would introduce other inaccuracies inherent in the use of a sensitive electroscope, which fails entirely, for example, in boisterous weather. As a consequence, readings were made on the same instrument without any variation which bore a ratio to each other in some cases of 20 : 1. The carbon plate C was finally connected to a potential divider, usually a divided megohm across which a battery was connected. The potential of C was not greater than 15 volts above or below that of S, which was maintained at earth potential.

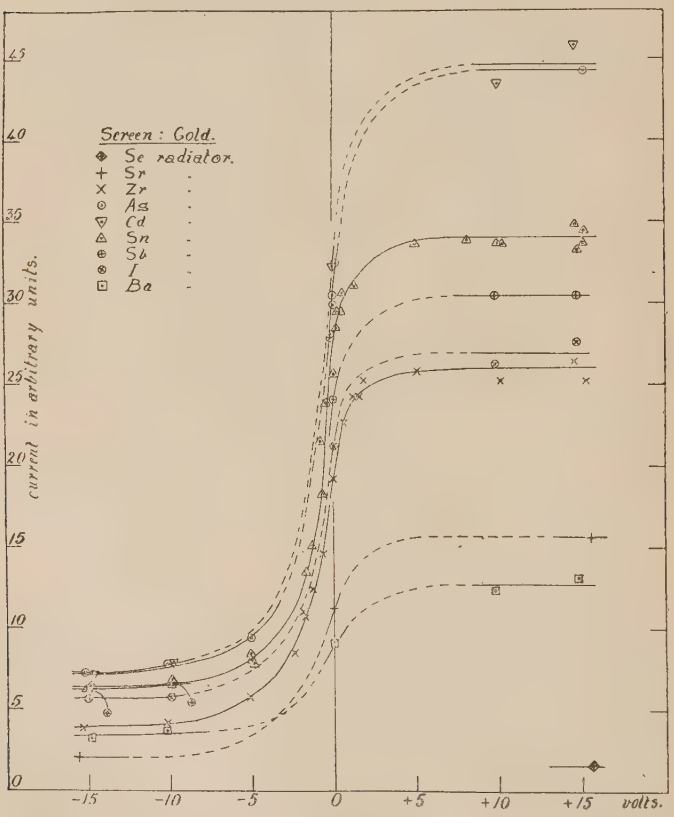
The electrons emerged from an area of S, 3 cm. in diameter, into the evacuated space between S and C, 2 mm. deep and 11·4 cm. in diameter, and the curves of the charge acquired by S in a given standard of time against the difference of potential between C and S should give a measure of the number of electrons emerging with a normal component of the energy greater than that given by this difference of potential, though undoubtedly some of the electrons are lost at the boundary. Finally, it should be stated that no measurable reading could be obtained if either the secondary radiator were removed or if the gold screen were replaced by a carbon plate.

* Phil. Mag. xlvi. p. 475 (1923).

Experimental Results.

Taking the greatest precautions, therefore, that conditions should be the same in all cases, fig. 2 shows the resulting curves for 9 secondary radiators used separately, the ordinates representing the positive charge acquired by S in 4 minutes, being proportional to the number of electrons emerging per second from S whose normal energy component exceeds eV when V is the potential of C.

Fig. 2.



After a careful examination of many of these curves, using different radiators and even different screens, I have concluded that the only variations they show amongst themselves are the maximum and minimum values of the electron currents, and these are intimately connected with the wave-length of the X-radiation producing them. The maximum electron emission seems to be reached at a positive potential

of C numerically smaller than the negative potential of C giving the minimum electron emission, and neither exceeds about 15 volts. Great changes in the ordinates do not occur for correspondingly large changes of potential above +15 volts or below −15 volts. All the curves seem to rise to the axis V = 0 very steeply and in a similar manner—in fact, by far the greater number of the electrons have a velocity of only a few volts, nor does this seem to change very much over the one and a half octaves of X-rays employed in these experiments. The conclusions drawn are (*a*) the difference between the maximum and minimum ordinates for each curve measures the number of the δ- or slow rays, and (*b*) the minimum ordinate measures the totally distinct group of true photo-electrons or β-rays possessing very much greater energy. So slowly moving are many of the δ-particles that a positive potential is required to remove many from the surface film of the metal.

Fig. 3.

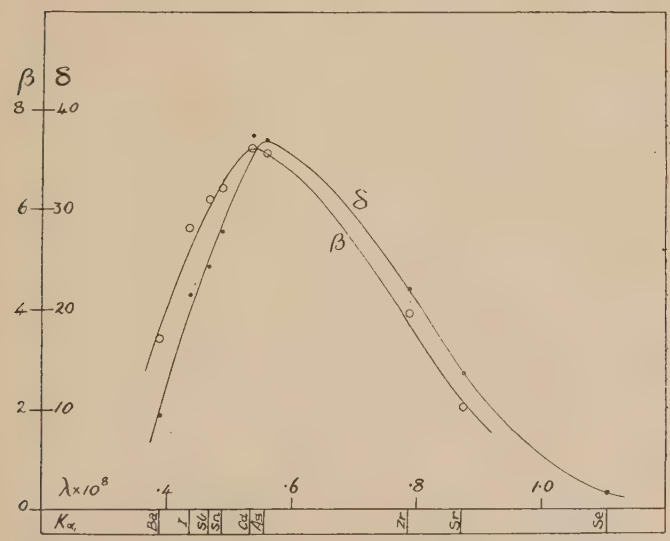


Fig. 3 shows the result of plotting (*a*) the differences between maximum and minimum ordinates, (*b*) the minimum ordinates against the wave-length of the X-rays falling on the gold film, the curve marked β being the minima and that marked δ the difference between the maxima and minima. The ordinates of the β curve are magnified 5 times. The data are given in the table.

Electronic Emissions from a Gold Film.

Incident X-rays from	At. No.	$\lambda_{K_{\alpha_1}} \times 10^8$ cm.	Numbers relative and uncorrected for absorption of incident X-rays by experimental vessel. β-rays.	δ-rays.
Se	34	1·104	—	c. 1·7
Sr	38	·871	2·0	13·6
Zr	40	·788	3·9	22·1
Ag	47	·558	7·1	37·1
Cd	48	·534	7·2	37·4
Sn	50	·489	6·4	27·6
Sb	51	·468	6·2	24·2
I	53	·437	5·6	21·3
Ba	56	·388	3·4	9·3

The curves obviously show the characteristic shape of the intensity distribution curves for the X-radiation from a Coolidge tube obtained by the method of crystal reflexion into an ionization chamber * before correction is made for absorption in the crystal.

The β- and δ-rays therefore show the following characteristics: (*a*) the numbers of β- and of δ-rays emitted from a thin film of gold exposed to X-rays of various wave-lengths are distributed amongst wave-lengths in a manner similar to the distribution of energy amongst wave-lengths obtained by the ionization chamber using crystal reflexion; (*b*) there is no constant proportionality between the number of δ-rays and the number of β-rays for varying wave-lengths of incident X-rays. The ratio of δ-rays to β-rays emitted per sq. cm. decreases rapidly according to a complex function as the wave-length of the incident X-rays decreases.

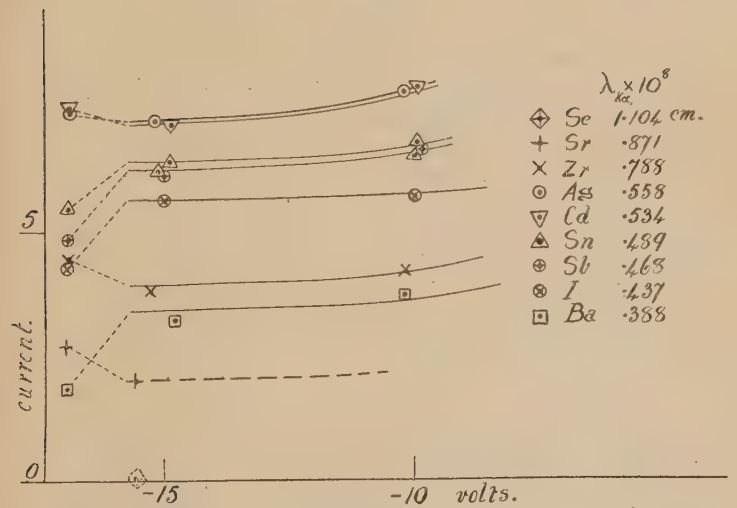
There would, however, be strict proportionality between the β- and δ-rays emerging from the gold film if each were produced by quasi-independent X-ray beams, always of the same relative intensities as measured by the number of electrons associated with each but differing in wave-length by a constant amount as the spectrum is traversed. This difference of wave-length from the graph (fig. 3) amounts to 0·040 A.U., the δ-rays being produced by the longer wave-lengths.

In drawing the curves for fig. 3, no attempt has been made to correct for absorption in the aluminium and carbon through which the incident rays have to pass on their way to the gold film.

* Hull, Phys. Rev. i. p. 156 (1916); Duane & Hunt, Phys. Rev. ii. p. 166 (1915); Ledoux-Lebard et Douvillier, *C. R.* 1916.

Fig. 4, which represents the bottom left-hand corner of fig. 2, has been added in order to show that the relative displacement of the two curves for what I have called the β-rays and δ-rays could scarcely have been brought about by a consistent error, if such existed, in the readings of the smaller currents. The points in the vertical row on the left of this figure indicate where the current-potential curves should terminate if the ratio between the numbers of δ-rays and β-rays were maintained constant and equal to 5 : 1 as the gold film was subjected to X-rays of increasing wave-length ; in other words, if the two curves of fig. 3 coincided.

Fig. 4.



The displacements are well outside the limits of experimental error in this region and, moreover, some are up and others are down. Once again, we should not expect fluctuations of this nature from the influence of the successive changes of energy of the groups of β-rays emerging from the gold film under the influence of the range of wave-lengths employed, as it lies well within the region L_{α_1} to K_{α_1} for gold.

Another point worth noting is that the emission of slow particles, thermions for example, is influenced very largely by the physical treatment of the surface of the substance emitting. No baking-out treatment has been possible. A clear indication, however, that the class of phenomenon described is a function of the metal of the screen and not of the gaseous film upon it, nor of the residual gas around it, is shown by replacing the gold film by one of another metal.

The δ-ray current fell to 5·8 on the same scale for a silver film, and to 2 for a tin film, using Cd K_{α_1} rays. In these last results, however, a further complication is introduced by the proximity of the K_{α_1} lines for silver and tin with that of the incident K_{α_1} line for cadmium.

If we leave out of account the transformations that must occur at the secondary radiator and the effect of the X-radiations scattered in their passage through the aluminium and carbon bottom of the experimental vessel, and consider only the X-radiations scattered in all directions either by the gold film or by the paraffin-wax and lead behind it (though from previous work I am inclined to think that the former of these two is the more important), then the curves of fig. 3 give a measure of the total numbers of particles of the two types emerging at all angles ranging from 180° to 90° to the direction of the incident beam, and they obviously have different associations. Associating the curve for β-rays with Compton's unmodified scattered X-rays, and that for δ-rays with the modified scattered X-rays, the mean change in wave-length should be given by the expression $0{\cdot}048 \times$ (mean value of $\sin^2\theta/2$), where θ ranges over from 180° to 90° $= 0{\cdot}040$ Å.U., whilst it is remarkable that the best value I can obtain from the shift between the two curves of fig. 3 is also 0·040 Å.U. Herein may also lie the explanation of the well-known asymmetric distribution of the so-called secondary electronic radiations about a radiator.

Summary.

The numbers of δ-rays and β-rays emerging from the face of incidence of X-rays of varying wave-length upon an extremely thin gold film have been plotted against wave-length. The curves show that there would be strict proportionality between the δ-rays and the β-rays if each were produced by quasi-independent X-ray beams rising and falling with one another in intensity, but differing in wave-length by an amount equal to 0·040 Å.U., the δ-rays being associated with the longer wave-lengths. This is exactly the amount we should expect from the quantum theory of scattering of X-rays developed recently by Compton, if the δ- and β-rays can be associated respectively with the modified scattered and the unmodified scattered X-rays.

My thanks are due to the Governors of Birkbeck College for a grant in aid of this research.

Birkbeck College
(University of London), E.C. 4.

XXIX. *The Fine Structure of the Nitrogen, Oxygen, and Fluorine Lines in the Extreme Ultra-violet.* *By* I. S. Bowen *and* R. A. Millikan, *Norman Bridge Laboratory of Physics, California Institute of Technology, Pasadena* *.

[Plate IX.]

IN the preceding studies † which carried the region of ultra-violet wave-lengths explored by vacuum grating spectroscopy down to 136 Å., our primary aim was to find what lines existed in this hitherto unexplored region, and it is altogether obvious, therefore, that we were purposely sacrificing resolution to intensity.

In order, however, to obtain the most certain interpretation of the new lines, *i. e.*, to find the optical series to which they belong, and hence the kind of ionization existing in the atoms giving rise to them, it became necessary to arrange the experimental conditions so as to be able to study with as high resolution as possible the fine structure of these lines. The reason that such a study was not at first desirable, nor, indeed, possible, is found in the fact that in order to obtain the best resolution it is necessary to go to spectra of a high order, but in order to be able to recognize a line of given wave-length in one of its high orders it is first necessary to measure, approximately at least, that wave-length by work in the first order. Such fine structure work as we are now doing, therefore, necessarily followed after such exploring work as we have already reported.

The accompanying results are obtained with "hot-spark" high-vacuum spectrometry, using a slit width of ·02 mm., a 4-inch grating of 1 m. focus, with which spectra on Schumann plates in spectral orders *up to and including the tenth* have been obtained. These results represent both the highest resolution and the highest precision of wave-length determination by far which we or, so far as we know, others have as yet obtained in the region below 1000 Å.

It is estimated that the separations reported herewith may be relied upon to about ·01 Å., while the absolute values of the wave-lengths may possibly be in error, on account of the uncertainty in the standards of comparison, by slightly more than this. This means that the precision of our previously published wave-lengths has been multiplied in the present work by about tenfold, and that *a set of wave-length standards correct to a few hundredths angstroms has been established in*

* Communicated by the Authors.

† Millikan and Bowen, Phys. Rev. xxiii. p. 1 (1924).

the region below 1000 Å. *where no such standards have hitherto existed.* In the region above 1000 Å. the accompanying wave-lengths are somewhat less reliable because of our inability to work in higher than the third spectral order with these lines of longer wave-length.

These results could not have been obtained had not Dr. J. A. Anderson ruled for us at the Mount Wilson Observatory, in accordance with our specifications, a new 4-inch grating of very unusual quality.

Our first purpose in using as high resolution as possible was to obtain evidence as to whether the very strong oxygen line at 834·0 Å. and also the strong nitrogen line at 1085·2 were not due to atoms stripped of all their valence electrons; for we had already obtained excellent evidence * that the strongest lines in our "hot spark" were due to atoms from which the valence electrons had all been stripped off in the case of Na, Mg, Al, Si, and P, as well as in the case of Li, Be, B, and C, and we at first inferred that the very strong 834·0 oxygen line and the 1085·2 nitrogen line arose in the same way. If so, these lines all had of necessity to be doublets, since stripped atoms must all give spectra of the alkali type. Fig. 1 of the Plate presents a photograph in the fifth order, showing clearly the seven components which this line has revealed when analysed with sufficient resolution. This same structure has now been clearly shown in photographs taken in the second, third, fourth, fifth, sixth, and seventh orders. The magnification in fig. 1 is about thirtyfold.

The precision of about ·01 Å. obtained in locating the components of this line is due to the fact that its fifth order fell close to the well-known standard barium line, the wave-length of which Fowler gives as $\lambda = 4130{\cdot}68$ Å. The second order of our new boron line at 2066·41 and 2067·88 also comes exceedingly close to this standard barium line, thus enabling this strong boron line to be used as a secondary standard.

The other lines which were used as standards with which to compare some of the orders of the lines whose wave-lengths were sought were the aluminium doublets at 1854·67 and 1858·13, and at 1935·83 and 1990·50; the carbon line at 2297·59, and the second order of the hydrogen line at 1215·68.

Plate IX. also shows a very satisfactory photograph of the structure of the strong nitrogen line at 1085·2, which is here

* Phys. Rev. xxiii. p. 33 (1924).

revealed as a quadruplet. *Neither of these two lines,* 834·0 *or* 1085·2, *is then due to stripped atoms.*

TABLE I.

Oxygen.

Int.	λ I. A. Vac.	ν.
1	507·45	197063·7
1	507·73	196955·1
1	508·23	196761·3
1	525·82	190179·1
1	553·33	180724·0
1	554·07	180482·6
1	554·52	180336·1
1	555·23	180105·5
2	599·60	166777·9
1	608·41	164362·8
1	609·85	163974·7
1	610·06	163918·3
1	610·79	163722·4
1	629·75	158794·8
1	644·17	155238·5
2	702·36	142377·1
3	702·89	142269·8
3	703·90	142067·1
3	718·56	139167·2
1	779·86	128228·1
2	787·74	126945·4
2	790·22	126547·0
1	796·69	125519·3
3	832·78	120079·7
3	832·95	120055·2
4	833·35	119997·6
4	833·77	119937·2
4	834·48	119835·1
2	835·12	119743·3
4	835·31	119717·2

Nitrogen.

Int.	λ I. A. Vac.	ν.
1	685·04	145976·9
1	685·55	145868·3
1	685·86	145802·4
1	686·39	145689·8
1	763·37	130998·1
1	764·39	130823·3
1	765·21	130683·1
1	771·59	129602·5
1	771·97	129538·7
1	772·45	129454·9
1	772·97	129371·1
1	915·71	109204·9
1	916·13	109154·8
2	916·82	109072·7
2	989·90	101020·3
3	991·66	100841·0
3	1084·04	92247·5
4	1084·60	92199·9
3	1085·59	92115·8
4	1085·75	92102·2
1	1134·20	88167·9
1	1134·45	88148·4
1	1135·02	88104·2
2	1492·83	66986·9
2	1494·78	66899·5

Fluorine.

605·64	165114·6
606·23	164955·5
606·83	164790·8
607·43	164628·0
607·99	164476·4
656·00	152439·0
656·34	152360·1
656·84	152244·1
657·69	152047·3
658·31	151904·1

Table I. shows the structure and wave-length of all save the very weakest of the oxygen, nitrogen, and fluorine lines

which appear upon our plates. It will be seen that the frequency separation of the lines of the 507 triplet is quite the same as that of the 703 triplet, thus indicating an identity of origin—an origin which will be shown in a later paper to be O_{III}.

The structure of the two fluorine lines is not as certain as are the other structures shown.

Table I. contains the fine structure of all of the strong lines of wave-length below 1500 Å. which are due to any of the atoms up to neon, except those due to carbon and to boron. The fine structures of all the boron lines have been analysed in a preceding paper * and definitely assigned to B_{III}, B_{II}, and B_I.

As to the strong lines of carbon, previous to this analysis with high resolution we had been inclined to regard the very powerful carbon line at 1335 Å. as arising from the stripped atom of carbon, for it had been found to be a doublet, and it also had other characteristics which we had associated with stripped atoms †. Doubt had been thrown upon this conclusion, however, by the fact that Simeon ‡ had obtained this line in both a 30-volt arc and a 40-volt arc, and such an arc should not give rise to a stripped atom of carbon. A further comparison of the intensities of the 1335 doublet with the 1550 carbon doublet brought out quite convincing evidence that it was the latter instead of the former which had its origin in the stripped atom of carbon.

This argument, from the point of view of intensity, is contained in the following table :—

Table II.

Line.	Old.	New.	Simeon.			Hutchinson.	
			220 v.	40 v.	30 v.	H.-spk.	110 v. arc.
1335	15	2, 6, 5, 5, 4, 2	10	Obs.	Obs.	8	10
1550	5	4, 5, 6, 5, 5, 3	3	...	...	3	...

The column labelled "old" represents results obtained with electrodes of carbon which could be separated as much as 2 or 3 mm. and which gave sparks having a rather "arc-like" character, while the columns headed "new" correspond to observations made with aluminium electrodes in which carbon was merely an impurity. The spark here passed with difficulty and was a true "hot spark." It is to

* Proc. Nat. Acad. Sci. May 15, 1924.
† Phys. Rev. xxiii. p. 33 (1924).
‡ Proc. Roy. Soc. civ. p. 373 (1923).

be noted that in all these new observations the 1550 line has gained largely in intensity relative to the 1335 line, being actually the stronger line in most of them. *Line* 1550 Å. *thus clearly corresponds to a higher state of ionization than does line* 1335 Å. Also Simeon's * and Hutchinson's † data are consistent in revealing the 1335 line in arcs, while it is only in the "high potential arc" or the hot spark that the 1550 line appears at all.

The foregoing evidence is beautifully supported by the progression of the doublet separation of the $p_1\ p_2$ terms shown by the stripped-atom spectra in the group of elements from lithium to carbon shown in Table III. The 1335 line does

TABLE III.

	$\lambda(2s-2p)$.	ν.	Differences.	$\Delta\nu$.	$\frac{\Delta\nu}{(N-2)^4}$.
Li	6707·85	14903·8		·338	·338
			17023·8		
Be	3131·194	31927·60		6·61	·413
	3130·546	31934·21	16431·1		
B	2067·88	48358·7		34·4	·425
	2066·41	48393·1	16122·5		
C	1550·84	64481·2		107·4	·420
	1548·26	64588·6			

not fit into this progression at all, as does the 1550 line, for its doublet separation $\Delta\nu$ is 67 instead of 107, which makes the corresponding number of the last column come out ·262 instead of ·420, the latter of which alone is consistent with the other numbers given in this last column. Also the equality of "differences" shown in the fourth column is entirely destroyed if line 1335 is inserted in place of line 1550.

The doublet separation shown in the last two columns of the table not only increases as the fourth power of the effective nuclear charge, but its numerical value is closely predicted by the relativity, or regular, doublet law, which is already known to give the separation of the regular X-ray doublets.

The linear progression of frequencies shown in the fourth column is a result of the fact that the separation of the s and p terms in all these spectra follows the law of the irregular X-ray doublet. Indeed, we have found by a study with high resolution like that shown in the plate, of the fine structure of the doublets and triplets in our extreme ultra-violet spectra, *that the X-ray doublet laws are applicable to the whole field of optics as well as to that of X-rays.*

* Simeon, Proc. Roy. Soc. civ. p. 373 (1923).

† Hutchinson, Astro. Phys. Jr. lviii. p. 291 (1923).

We have also obtained unimpeachable proof that our "hot spark" produces the whole series of stripped atoms L_I, Be_{II}, B_{III}, C_{IV}, N_V; also Na_I, Mg_{II}, Al_{III}, Si_{IV}, P_V, Si_{VI}, as well as other series of similar atomic structure like B_I, C_{II}, N_{III}, O_{IV}. *Indeed, we have definitely identified lines due to all of the foregoing atoms.* The analysis leading to these conclusions is to appear in detail in a forthcoming paper in the 'Physical Review,' entitled "The Extension of the X-Ray Doublet Laws into the Field of Optics." The main purpose of the present paper is to show the sort of resolution and the accuracy of wave-length determination which we are attaining in the new studies which we are now making of all the stronger lines, the wave-lengths of which we had located approximately in our preceding studies of extreme ultra-violet spectra.

XXX. *Surface Tension of Colloidal Solutions and Dimensions of certain Organic Molecules.* *By* P. Lecomte du Noüy, *Sc.D.**

[From the Laboratories of the Rockefeller Institute for Medical Research.]

A LARGE number of papers have been published on the surface tension of colloidal solutions; but, owing to the methods used, certain facts have been overlooked so far. The purpose of this paper is to review briefly the results obtained by using a different method, namely, the pull on a ring. By this method, the surface tension of the same layer of liquids may be measured, at intervals of time, instead of that of a continuously renewed layer †.

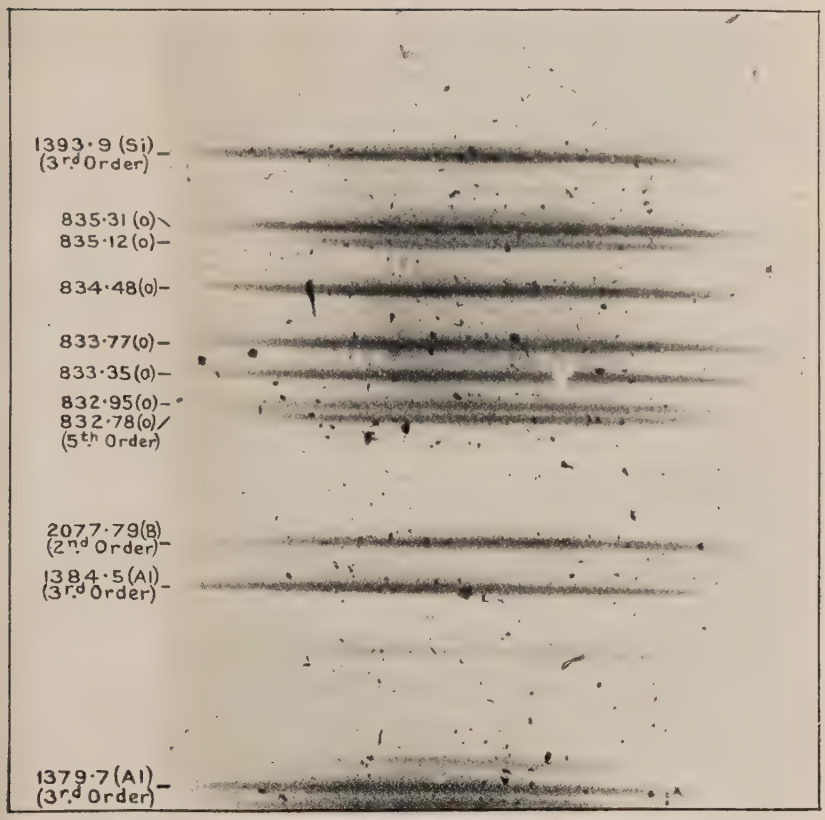
Experimental.

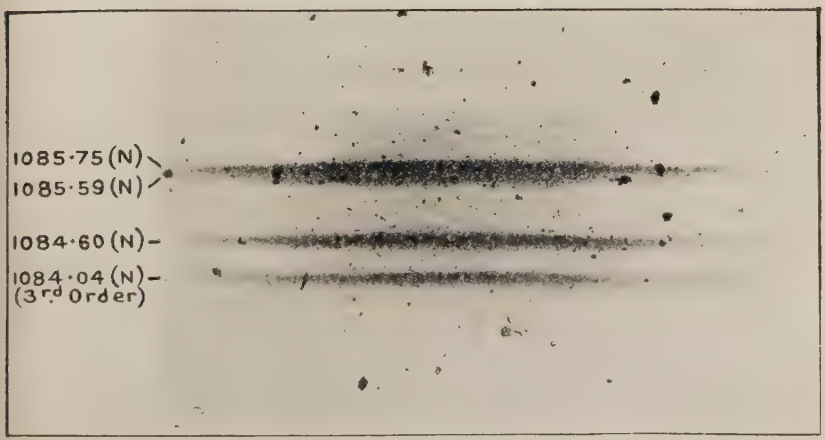
It will suffice to say that the instrument used, based on the work of Weinberg ‡, has been described by the writer

* Communicated by the Author.

† du Noüy, P. L., J. Exp. Med. xxxv. pp. 575, 707; xxxvi. pp. 115, 547 (1922); xxxvii. p. 659; xxxviii. p. 87 (1923); xxxix. p. 37 (1924). ("Surface Tension of Serum, VIII. Further Evidence on the Existence of a Superficial Polarized Layer of Molecules at Certain Dilutions.") J. Exp. Med. 1924, in press.—("Surface Tension of Serum, X. On the Thickness of the Monomolecular Layer of Serum.") J. Exp. Med. 1924, in press.—("On the Surface Tension of Colloidal Solutions and the Size of Some Colloidal Molecules.") Read before the American Physical Society, Feb. 23, 1924, in press.

‡ Weinberg, B., *Zeit. f. Phys. Chem.* x. p. 34 (1902).


1393·9 (Si)
(3rd Order)
835·31 (O)
835·12 (O)
834·48 (O)
833·77 (O)
833·35 (O)
832·95 (O)
832·78 (O)
(5th Order)
2077·79 (B)
(2nd Order)
1384·5 (Al)
(3rd Order)
1379·7 (Al)
(3rd Order)


1085·75 (N)
1085·59 (N)
1084·60 (N)
1084·04 (N)
(3rd Order)

in the 'Journal of General Physiology'*, by Sir William Bayliss†, and by Holmes‡. The torsion of a wire controlled by a worm-gear is used to counteract the stress of the liquid film adhering to a platinum ring, and as the amount of torsion can be measured by a simple reading on a dial, the surface tension is measured directly. The measurements require only 20 seconds. Those reported in this paper were made at a temperature of $23 \pm 0{\cdot}5°$ C. Two cubic centimetres of liquid in watch-glasses were used, the diameter of the free surface being very nearly 4 cm. The glassware, containers, flasks, pipettes, watch-glasses, etc., were freshly boiled for two hours in a cleaning solution (sulphuric acid and potassium dichromate), rinsed in specially prepared distilled water, and dried. No alcohol or ether was ever used. When NaCl was used for preparing the solutions of serum, for example, it was washed, then recrystallized twice. The greatest care was taken in handling the solutions under experiment, so as not to disturb their surface. A special table was built on which the surface tension apparatus, supported on a small carriage, was rolled on rigid rails, in front of every solution in succession. Under such conditions about 38,000 measurements were made, and the following results, which will be summarized rapidly, were obtained.

I. The surface tension of colloidal solutions is not constant but decreases rapidly as a function of the time. So far, no colloidal solutions have been found which do not show this phenomenon. Experiments have been carried out mainly with blood serum, pure albumen, hemoglobin, globulins, sodium oleate, sodium glycocholate and taurocholate, and saponin solutions, a great number of dyes, and gold, silver, copper, and iron sols (electrically prepared). The drop varies, of course, according to the substances and to the concentration. It is much smaller in the electrosols mentioned above. At a given concentration, it can be expressed by the formula (figs. 1 and 2)

$$\gamma = \gamma_0 e^{-Kt^{\frac{1}{3}}},$$

until a certain stable value is attained. This phenomenon is due to the adsorption in the surface layer, in function of time, of the molecules in suspension. As the concentration of the solution in every watch-glass does not vary, this phenomenon seems to differ from ordinary adsorption which

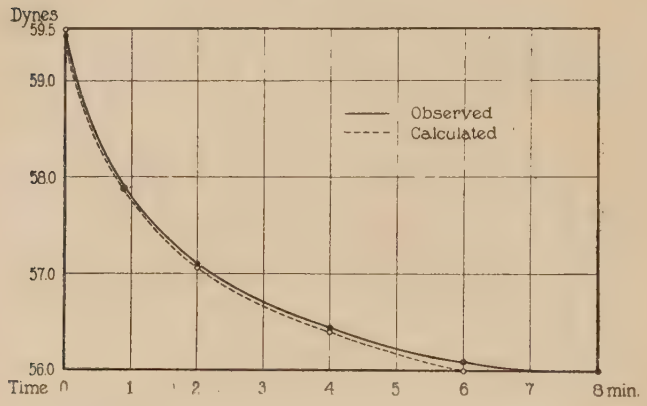
* du Noüy, P. L., J. Gen. Physiol. i. p. 521 (1919)

† Sir William Bayliss, 'The Colloidal State,' London, 1923, p. 65.

‡ Holmes, H. N., 'Laboratory Manual of Colloidal Chemistry,' New York, 1922, p. 52.

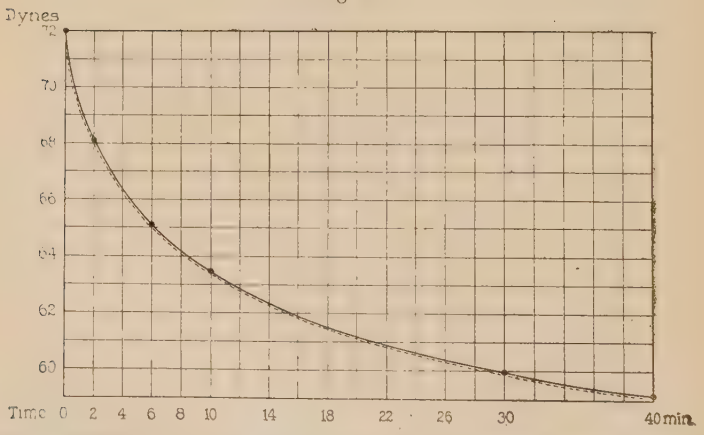
is regarded as almost instantaneous. However, it may be assumed that in these colloidal solutions the concentration varies proportionally to the time as the adsorption progresses.

Fig. 1.



Drop of surface tension of pure blood serum (rabbit).

Fig. 2.

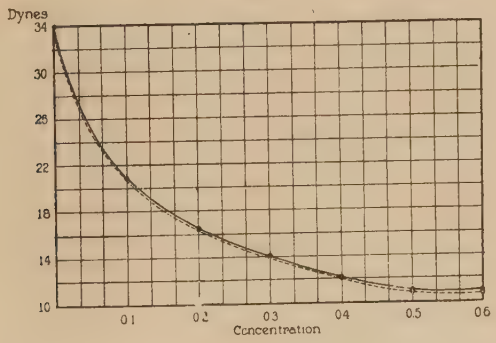


Drop of surface tension of a solution of 1/10 blood serum (rabbit). Dotted line is calculated according to the formula $\gamma = \gamma_0 e^{-Kt^{\frac{1}{2}}}$.

This assumption is supported by the fact that the same formula, in which t is replaced by c (concentration), satisfactorily fits such adsorption isotherms as published by

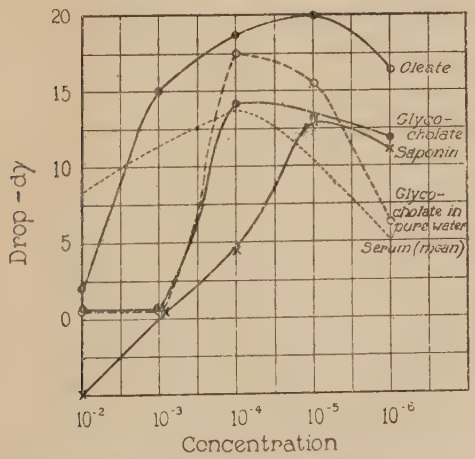
Lewis *, expressing the adsorption of sodium glycocholate by paraffin oil (Table I. and figs. 1 and 3). Fig. 4 gives an

Fig. 3.



Action on s urface tension of adsorption of sodium glycocholate by paraffin oil (Lewis).

Fig. 4.



Time-drop of the surface tension of certain colloidal solutions, in function of their concentration.

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* Lewis, W. C. McC., Proc. Physic. Soc. xxi. p. 150 (1909); Phil. Mag. xvii. p. 466 (1909); *Zeit. Chem. u. Indust. Kolloide*, v. p. 91 (1909): also cited by Willows, R. S., and Hatschek, E., 'Surface Tension and Surface Energy, and their Influence on Chemical Phenomena.' Philadelphia, 1915, p. 41.

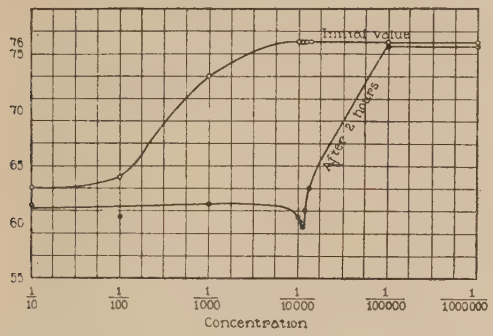
idea of the phenomenon as a function of the concentration for a few substances. It is to be noticed that a sodium oleate solution in such quantities as 10^{-5}, although it affects the initial surface tension of water very little, will cause a drop of more than 25 dynes in two hours. The drop in the surface tension of sodium oleate at higher concentrations has been observed before, but could not be followed step by step on account of the methods used, and was not thought to be a general phenomenon of colloids. The effect of dilution was also overlooked. One-millionth part of sodium oleate does not affect the initial surface tension of water, but causes a drop of 20 dynes in two hours. The drop weight or drop count methods are unable to show this phenomenon.

II. In all the cases studied (organic colloids), a decided minimum value was observed at a given concentration. Under the conditions of our experiments, it occurred around 1/750,000 for sodium oleate, 1/117,200 for crystalline egg albumen, and 1/10,500 for rabbit serum, and as this serum contained 6·51 per cent. of proteins, the final dilution was near 1/160,000. On both sides of this minimum (fig. 5) the drop is smaller. In the case of certain strongly active substances (saponin, etc.), it often happens that, at low dilutions (1/10 to 1/1000), a slight increase is observed instead of a drop. An hypothesis was made in order to account for the maximum drop. At this optimum concentration (the size and shape of the vessels in which the solutions were exposed being taken into consideration), the existence of a monomolecular and oriented layer was assumed ; such a layer is only possible at one concentration for every orientation of the molecule in the same vessels, and its geometric organization would account for the existence of the smallest possible field of forces compatible with the number of free molecules in the solution. Figs. 5 and 6 show how well defined and sharp this minimum is in the case of serum and sodium oleate. A more careful investigation on both sides of this minimum revealed the presence of two more minima. One of these probably corresponds to a monolayer (the writer proposes this term instead of " monomolecular layer ") of horizontal molecules. Experiments are being carried out on this subject at present.

III. If the solutions are stirred, even slightly, after standing, the surface tension rises and reaches a value generally smaller than the initial value (fig. 7). This phenomenon can be repeated a number of times, and for this

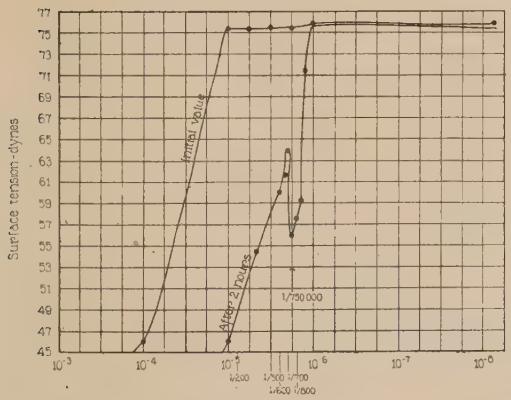
very reason great care must be taken when the time-drop is being measured. In the case of the biological colloids (blood

Fig. 5.



Initial values and values after two hours of the surface tension of solutions of serum.

Fig. 6.

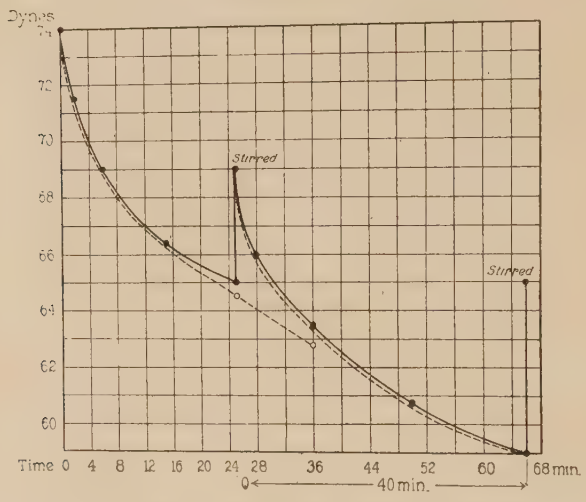


Initial values and values after two hours of the surface tension of sodium oleate solutions in water. Between 10^{-5} and 10^{-6}, the figures representing concentrations should be divided by 1000, namely, $\frac{1}{200,000}$, $\frac{1}{500,000}$, etc. Space did not allow more figures on the chart.

serum) studied, after some time (48 hours), the solution became practically inert when it had been stirred frequently and there was no further rise after stirring.

IV. Should the above assumption of the existence of a homogeneous oriented monolayer at a given concentration be well founded, the rate of evaporation of such a solution should be slower than that of any other concentration.

Fig. 7.



Rise in surface tension when solution is stirred.

Water molecules would not escape so freely from a solution covered with such a film. At a higher concentration, we have assumed that there is a piling up, and no organization of the molecules. Therefore, the water molecules can pass between and escape more easily than through a closely-fitting mesh of identically oriented molecules. At lower dilutions, the breaks in the film would allow the normal process of evaporation to take place. Experiments proved that, with the colloidal solution tested (blood serum), such was the case. The results of a series of experiments are given in Tables II. and III.

So far, our assumption seems to be supported by the facts. It is very plain in these tables that solutions at 1/10,000 evaporated more slowly than the others. An interesting conclusion may be drawn from these experiments on serum. Of course, the critical concentration 10^{-4} is a function, among other things, of the ratio $\frac{\text{surface}}{\text{volume}}$ of the vessels in which the solutions are exposed. In the case of our watch-glasses, this ratio is 12, if it is assumed that adsorption takes

TABLE I.

Agreement between Figures Observed and Calculated for the Lowering of Surface Tension at the Interface between a Solution of Sodium Glycocholate and Paraffin Oil, in Function of the Concentration (fig. 3).

$K = 0{\cdot}222$.

Concentration, per cent.	0	0·1	0·2	0·3	0·4	0·5	0·6
Surface tension observed (Lewis), dynes	34·0	21·0	16·5	14·0	12·2	11·0	10·9
Surface tension calculated $\gamma = \gamma_0 e^{-Kc^{\frac{1}{3}}}$, dynes	—	20·2	16·5	14·0	12·2	10·9	9·7

TABLE II. (ser. No. 1).

Diameter of Serum Solutions (Rabbit) evaporating in Watch-Glasses.

Dilution.	10^{-1}.	10^{-2}.	10^{-3}.	10^{-4}.	10^{-5}.	10^{-6}.
Diameter in mm. at 5.41 P.M., after 6 hours' evaporation	26	27	27	30	27	26
30 minutes later	20	20	23	26·5	23	22
1 hour later	0	0	6	14	0	0

TABLE III. (ser. No. 2).

Diameter of Serum Solutions (Rabbit) evaporating in Watch-Glasses.

Dilution.	10^{-1}.	10^{-2}.	10^{-3}.	10^{-4}.	10^{-5}.	10^{-6}.
Diameter in mm. at 5·42 P.M.	18	23	21	21	20	20
50 minutes later	0	5	8	12	0	0

place on the glass, as will be shown later. Should the surface increase with respect to the volume (as happens when the volume decreases), this ratio would become very great. If we attempt to calculate the size of the vessels which would require pure serum to develop such a monolayer, in other words, in which the ratio $\frac{S}{V}$ would be equal to 134,000 instead of 12 (the serum being diluted to 1/11,000), it is found that they would have to be of the order of magnitude of the blood capillaries, filled with blood cells. Thus, one of the factors governing the concentration of colloids in the serum is found. The adsorption of molecules

of substances such as albumens and proteins in general (biological colloids) and sodium oleate takes place on the glass in a similar way as on the free liquid surface. This was ascertained in the following manner :—

Two series of watch-glasses were prepared ; in one series, 500 very small glass beads were placed side by side. The surface of the glass was thus increased by 14·2 sq. cm. The same set of solutions (rabbit serum at the following concentrations : 1/5000, 1/6000, 1/7000, 1/8000, 1/9000, 1/9500, 1/10,000, 1/10,500, 1/11,000, 1/11,500, 1/12,000, and 1/13,000) was placed in the two sets of watch-glasses. Without beads, the ratio $\frac{S}{V}$ equalled 12·8. With the beads, the volume of the liquid being the same, this ratio became 19·9. If our assumption is correct and provided adsorption takes place on the glass, the maximum drop must be shifted towards a higher concentration, and its place will be at a concentration $\frac{19{\cdot}9}{12{\cdot}8} = 1{\cdot}56$ greater, namely, at 1/7000 instead of 1/11,000. The experiments supported this view entirely, and the maximum drop, as well as the minimum value of the surface tension, occurred at 1/7000 in the watch-glasses with beads.

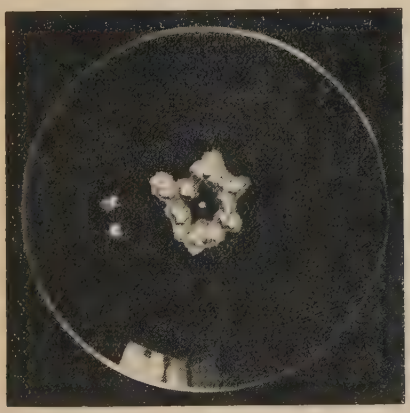
The existence of such a criterion (namely the minimum of surface tension) for a monolayer makes it possible to compute its thickness, if the concentration at which it occurs is accurately known. Fig. 5 shows that this value is very well defined. The specific gravity of anhydrous proteins of the serum was measured and found equal to 1·275. On such a basis, the thickness of a monolayer of serum proteins was found to be $38{\cdot}5 \times 10^{-8}$ cm. The length of the molecule of crystalline egg albumen was found to be $52{\cdot}8 \times 10^{-8}$, and if its molecular weight is assumed to be 34,000 (Sørensen), and Millikan's value for N, $6{\cdot}06 \times 10^{23}$, is taken, we find the square root of the cross-section of this molecule to be $29{\cdot}2 \times 10^{-8}$. Hence, it would seem to be oriented vertically. The same technique and calculation applied to a substance whose molecular weight is well known, such as sodium oleate, yielded the following figures (the minimum value of the surface tension occurs at 1/750,000, and the molecular weight is 304). The calculated length of the molecule is found to be $12{\cdot}3 \times 10^{-8}$ cm., and the square root of the cross-section $6{\cdot}8 \times 10^{-8}$ cm.

If we compare these figures with the dimensions of the

molecule of oleic acid, as given by Langmuir (length, $11{\cdot}2 \times 10^{-8}$; square root of cross-section, $6{\cdot}8 \times 10^{-8}$), we see that the diameter of the molecule is unchanged, but that its length is increased by $1{\cdot}1 \times 10^{-8}$ cm. This would correspond to the space occupied by the sodium atom at the end of the molecule. When the length of insoluble organic molecules (oleic acid, tripalmitine, tristearin, cetyl palmitate, myricyl alcohol, etc.) is divided by the number of carbon atoms, the length per carbon atom is obtained. The mean value of this length, for nine substances, is equal to $1{\cdot}4 \times 10^{-8}$ cm. As the sodium oleate molecule is dissociated, a double electric layer is probably formed at the surface, the free Na^+ ions being energetically attracted by the powerfully negative film due to the identical orientation of the oleic$^-$ ions in the surface layer.

V. When a solution of NaCl (0·9 per cent.) is allowed to crystallize in a perfectly clean watch-glass, the crystals are formed at the bottom and grow as evaporation takes place. They finally assume the appearance shown in fig. 8. When

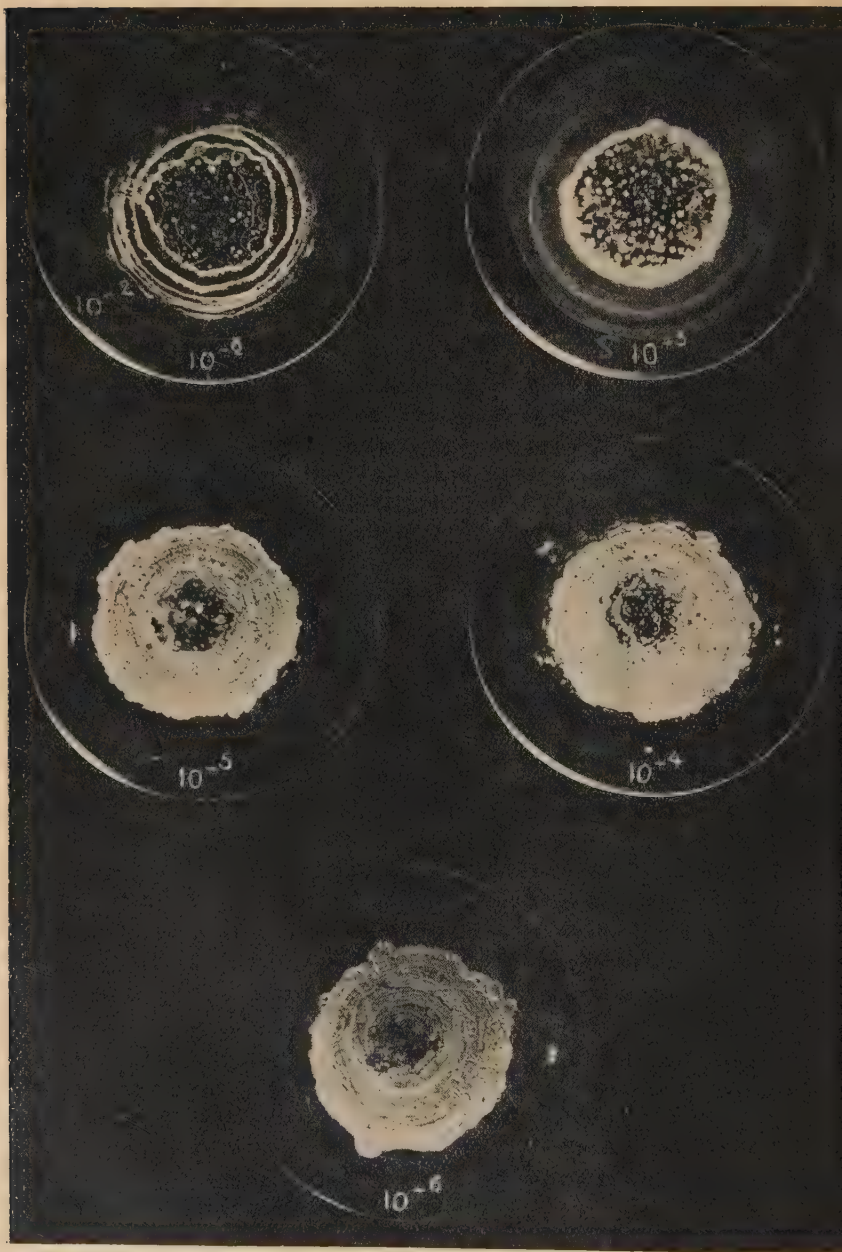
Fig. 8.



Crystals of pure sodium chloride : 2 c.c. of a 0·9 per cent. solution in a watch-glass.

a small amount of any colloid is added to such a solution, concentration in the bulk no longer takes place, large crystals are not formed, and the sodium chloride (or any other salt of the same kind) is deposited on the walls of the watch-glass in a thin, smooth, and often opaque, white layer of very small crystals (fig. 9). At the bottom, a darker area with a few tiny scattered crystals indicates that concentration did

Fig. 9.

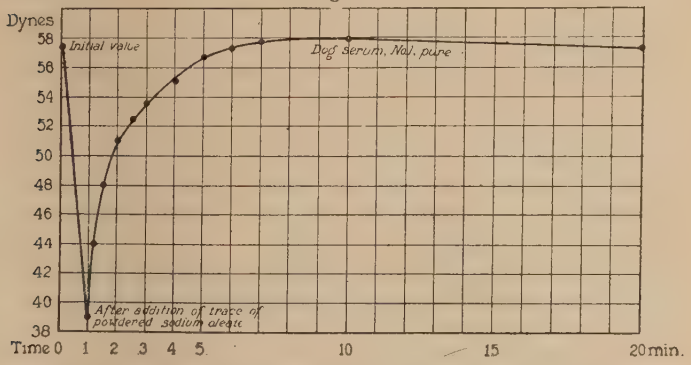


Sodium chloride crystals in watch-glasses. A small amount of saponin has been added to a 0·9 per cent. NaCl solution. The concentration of saponin is 10^{-2}, 10^{-3}, 10^{-4}, 10^{-5}, and 10^{-6}.

not take place, and that the molecules and ions are first being adsorbed on the colloidal micellæ, then carried up to the surface layer. As evaporation progresses, the colloidal particles, with their adsorbed NaCl, are deposited on the glass in concentric beaches. At certain concentrations, periodic rings are to be observed ; at 1/100, for example, in the case of serum, and 1/1000 for saponin and sodium oleate. The appearance of the crystals is quite characteristic of the concentration, and varies but little. Thus, in the case of a composite solution of colloids and crystalloids, Gibbs' law, which states that substances tending to increase surface tension will concentrate in the bulk, no longer holds true. This observation has thrown light on the spontaneous creation of membranes at interfaces which was difficult to explain before the discovery that not only colloids but also crystalloids concentrated in interfaces at the same time.

VI. When two colloids are present in the same solution, one of the factors governing the final surface tension of the

Fig. 10.



Recovery of the surface tension of a colloidal solution (dog serum pure) to which a trace of powdered sodium oleate was added.

solution is the adsorption equilibrium existing between the two. The following experiment will make this clear. If a trace of powdered sodium oleate (about 1/10,000 in weight) is added to a less surface-active colloid in solution, such as proteins, gelatin, gum arabic, or metallic sols, the surface tension drops instantaneously by about 50 per cent., then immediately starts rising again until a certain equilibrium (which may be called adsorption equilibrium) is attained. In certain cases (pure blood serum, for example), the final surface tension is equal to the original value before the addition of sodium oleate. In order to observe this phenomenon, measurements must be made every 30 seconds, or at least every minute (fig. 10).

The curve representing the phenomenon is again a logarithmic one. Let us call A the relatively inert colloid to which the surface active colloid B is added. When B is added in solution instead of powdered, or when the solution is stirred after its addition, the surface tension does not rise so high, as a greater number of micellæ of colloid A are coated with colloid B. When powdered sodium oleate (A) is added without stirring, a relatively small number of micellæ of colloid B are heavily coated with A, and in time practically all of A is adsorbed on a few B micellæ which either precipitate or collect in large aggregates with little action on surface tension. This buffing or antagonistic action of colloids seems to be a general phenomenon.

Summary.

The use of an instrument allowing measurements of the surface tension of the same layer of liquids at very short intervals (15 to 30 seconds) made it possible to study the evolution of certain surface tension phenomena in function of time, namely :

1. The spontaneous drop of the surface tension of all colloidal solutions, with the order of magnitude of 1 dyne per minute during the first minute. This drop increases with dilution and shows a maximum at a given concentration, varying between 10^{-4} and 10^{-5} generally. The drop may then reach 20 dynes for colloids such as blood serum and albumen, which were not considered as acting powerfully on the surface tension of water. Certain colloids, saponin, for instance, do not show any drop at high concentrations, but even a slight increase (10^{-1} to 10^{-3}).

2. When such solutions are stirred, the surface tension rises.

3. The existence of an accurate criterion of the existence of a monolayer at a well-known concentration makes the calculation of the thickness of such a layer possible. This criterion—minimum value—does not always coincide with the maximum drop. In the case of pure soluble substances (albumens, etc.), it gives the length of the molecule, and, when the molecular weight is known, its cross-section can be calculated. The length of the molecule of sodium oleate was found to be $12{\cdot}3 \times 10^{-8}$ cm. and its width $6{\cdot}8 \times 10^{-8}$ cm. The length of serum albumen was 43·3, and that of egg albumen $52{\cdot}8 \times 10^{-8}$ cm.

4. The crystallization of sodium chloride solution, or

other salts, is affected by even the presence of one-millionth part of most colloids, and large crystals do not form at the bottom of a watch-glass. On the contrary, as the ions are adsorbed on the surface, the NaCl molecules are deposited in fine crystals along the walls of the glass, and form periodic rings at certain concentrations.

5. Evaporation of serum solutions in watch-glasses is slower at a dilution of 10^{-4} than at any other concentration. This fact is explained by the assumption made in order to account for some phenomena reported above (1), namely, the existence of a monomolecular oriented layer at a given concentration.

6. When sodium oleate or any surface active colloid is added to another more inert colloidal solution, such as pure serum, for instance, the surface tension drops considerably, then rises immediately, and may reach its initial value in 7 minutes.

XXXI. *Central Orbits in Relativistic Dynamics treated by the Hamilton-Jacobi Method.* *By* G. Temple, *B.Sc., Birkbeck College* *.

Introduction.

THE first part of this paper is devoted to an exposition of a process of integration applicable in particle dynamics on any relativistic theory, and forming the appropriate generalization of the methods of Hamilton and Jacobi in classical mechanics. In the second part, this method is applied to the problems of planetary motion and of the deviation of rays of light in the solar field according to the theories of Einstein and Whitehead.

In the treatment of the Bohr hydrogen atom according to the restricted theory of relativity, Sommerfeld (14) and (15) has made use of this method, but so far it has not been employed in the general theory of relativity.

Canonical Equations for Particle Dynamics.

1. Let (x_1, x_2, x_3, x_4) be a "pure" system of coördinates, and let

$$ds^2 = \sum_{\mu,\nu} g_{\mu\nu}^{(x)} \cdot dx_\mu \cdot dx_\nu$$

be the fundamental differential form of the metric manifold.

* Communicated by Prof. A. N. Whitehead, F.R.S.

Then the equations to an historical route can be written in the form

$$x_\mu = x_\mu(\lambda), \quad \mu = 1, 2, 3, 4,$$

where the four functions $x_\mu(\lambda)$ are single-valued, differentiable, and satisfy the inequality

$$\sum_{\mu,\nu} g^{(x)}_{\mu\nu} \cdot dx_\mu(\lambda) \cdot dx_\nu(\lambda) \geqq 0.$$

Let

$$x'_\mu = \frac{dx_\mu(\lambda)}{d\lambda}, \quad \mu = 1, 2, 3, 4,$$

and let

$$\mathrm{E} = \sum_{\mu,\nu} \mathrm{J}^{(x)}_{\mu\nu} \cdot x'_\mu \cdot x'_\nu,$$

where $\| \mathrm{J}^{(x)}_{\nu\mu} \|$ is a symmetrical covariant tensor of the second order, and

$$d\mathrm{J}^2 = \sum_{\mu,\nu} \mathrm{J}^{(x)}_{\mu\nu} \cdot dx_\mu \cdot dx_\nu$$

is the fundamental differential invariant of the dynamic manifold.

The integral

$$\mathrm{I} = \int_{\lambda=\lambda_1}^{\lambda=\lambda_2} \mathrm{E} \cdot d\lambda$$

taken along an historical route joining the event-particles whose parameters are λ_1, λ_2 together with its first variation,

$$\delta \mathrm{I} = \int_{\lambda=\lambda_1}^{\lambda=\lambda_2} \sum_a \left(\frac{\partial \mathrm{E}}{\partial x_a} - \frac{d}{d\lambda} \cdot \frac{\partial \mathrm{E}}{\partial x'_a} \right) \delta x_a \cdot d\lambda + \sum_a \left[\frac{\partial \mathrm{E}}{\partial x'_a} \right]_{\lambda=\lambda_1}^{\lambda=\lambda_2},$$

is defined even when $d\mathrm{J} = 0$ and $\mathrm{E} = 0$.

If $d\mathrm{J} \neq 0$, we may identify the parameter λ with the integral

$$\int^{\lambda} d\mathrm{J}$$

taken along the historical route from some arbitrary fixed event-particle to the event-particle whose parameter is λ.

Then

$$\delta I = -2\int_{\lambda=\lambda_1}^{\lambda=\lambda_2} \sum_a \Big[\sum_\mu J^{(x)}_{\mu a}\,.\,\ddot{x}_\mu + \sum_{\mu,\nu} J \begin{bmatrix}\mu\nu\\ a\end{bmatrix}^{(x)}\,.\,\dot{x}_\mu\,.\,\dot{x}_\nu\Big]\delta x_a\,.\,d\lambda + \sum_a \Big[\frac{\partial E}{\partial \dot{x}_a}\Big]_{\lambda=\lambda_1}^{\lambda=\lambda_2},$$

where $$\dot{x}_\mu = \frac{dx_\mu}{dJ}, \quad \ddot{x} = \frac{d^2x_\mu}{dJ^2}.$$

Since $E = \left(\frac{dJ}{d\lambda}\right)^2$ the first variation of the integral will vanish if the functions $x_\mu(\lambda)$ are chosen to satisfy the equation

$$\sum_{\mu,\nu} J^{(x)}_{\mu\nu}\,.\,x'_\mu\,.\,x'_\nu = 0.$$

It has been shown in a paper by Murnaghan (1) that the functions satisfying this equation are the limiting forms assumed by the functions satisfying the more general equation

$$\delta I = 0,$$

as dJ (and E) tends towards zero.

This investigation is necessitated by the indeterminate character of the operator $\frac{d}{dJ}$ when $dJ = 0$.

2. Let $\|A^\sigma_{(x)}\|$ denote the components of the contravariant acceleration tensor

$$\Big\|\ddot{x}_\sigma + \sum_{\alpha,\beta} J \begin{Bmatrix}\alpha\beta\\ \sigma\end{Bmatrix}\dot{x}_\alpha\dot{x}_\beta\Big\|, \quad \sigma = 1, 2, 3, 4,$$

and let $\|F^{(x)}_\mu\|$ denote the components of the electromagnetic vector potential, which satisfy the equation

$$\sum_\mu \frac{\partial F^{(x)}_\mu}{\partial x_\mu} = \sum_{\mu,\rho} F^{(x)}_\rho\,.\,J \begin{Bmatrix}\mu\mu\\ \rho\end{Bmatrix}^{(x)}.$$

Let

$$F^{(x)}_{\alpha\beta} = \frac{\partial F^{(x)}_\alpha}{\partial x_\beta} - \frac{\partial F^{(x)}_\beta}{\partial x_\alpha}, \quad \alpha, \beta = 1, 2, 3, 4$$

and

$$F^{\sigma(x)}_\alpha = \sum_\beta J^{\beta\sigma}_{(x)}\,.\,F^{(x)}_{\alpha\beta}, \quad \alpha, \sigma = 1, 2, 3\ 4.$$

$\|J^{\mu\nu}_{(x)}\|$ being the contravariant associate of $\|J^{(x)}_{\mu\nu}\|$.

Then the equations of motion of a particle of proper mass m and charge e may be written in the form

$$m \cdot A^{\sigma}_{(x)} + \frac{e}{c} \sum_{\alpha} F^{\sigma(x)}_{\sigma} \dot{x}_{\alpha} = 0, \quad \sigma = 1, 2, 3, 4$$

in all theories of Relativity (c being a constant).

3. These equations are equivalent to equations (11) on p. 80 of 'The Principle of Relativity,' by A. N. Whitehead, and may be deduced, as in the book, as a condition of the vanishing of the first variation of the integral

$$\int_{\lambda=\lambda_1}^{\lambda=\lambda_2} \left(m \cdot dJ + \frac{e}{c} dF \right),$$

where

$$dF = \sum_{\mu} F^{(x)}_{\mu} \cdot dx_{\mu},$$

or of the integral

$$\int^{\lambda=\lambda_2} \left(\frac{m}{2} \sum_{\mu,\nu} J^{(x)}_{\mu\nu} \cdot \dot{x}_{\mu} \cdot \dot{x}_{\nu} \cdot dJ + \frac{e}{c} dF \right).$$

In view of the remarks of § 1 and of the investigation of the tracks of rays of light in the solar field which we shall make later, we shall use the second integral.

4. It has been remarked by Th. de Donder (2) that the equations to a geodesic of the dynamic manifold which are summarized in the formula

$$\delta \int_{\lambda=\lambda_1}^{\lambda=\lambda_2} dJ = 0$$

may also be written in the form

$$\frac{dx_{\alpha}}{dJ} = \frac{\partial W}{\partial u_{\alpha}}; \quad \frac{du_{\alpha}}{dJ} = -\frac{\partial W}{\partial x_{\alpha}}, \quad \alpha = 1, 2, 3, 4,$$

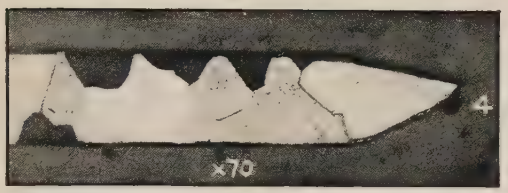
where

$$u_{\alpha} = \sum_{\mu} J^{(x)}_{\mu\alpha} \cdot \dot{x}_{\mu}, \quad \alpha = 1, 2, 3, 4$$

and

$$W = \sqrt{\sum_{\alpha,\beta} J^{\alpha\beta}_{(x)} \cdot u_{\alpha} \cdot u_{\beta}} \equiv 1.$$

5. Similarly it has been shown by W. Wilson (3) that the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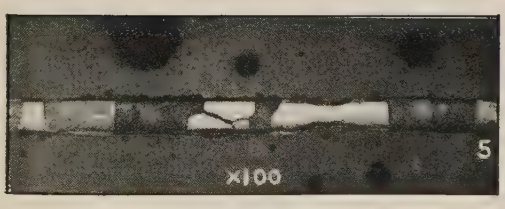
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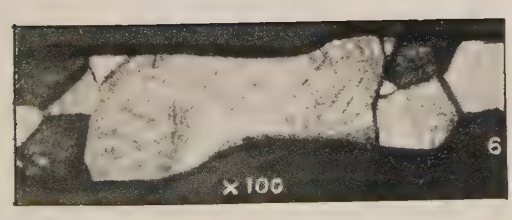
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equations of motions of a charged particle given above may be expressed in the form

$$\delta \int_{\lambda=\lambda_1}^{\lambda=\lambda_2} \sum_s \Pi_s . dx_s = 0,$$

where $$\Pi_s = m \sum_t J_{st}^{(x)} . \dot{x}_t + \frac{e}{c} F_s^{(x)}.$$

We now proceed to develop the ideas of the preceding sections along the lines suggested by the methods of Hamilton and Jacobi in classical mechanics.

6. The Lagrangian function L is defined by the equation

$$L = \frac{m}{2} \sum_{\alpha,\beta} J_{\alpha\beta}^{(x)} . \dot{x}_\alpha . \dot{x}_\beta + \frac{e}{c} \sum_\alpha F_\alpha^{(x)} . \dot{x}_\alpha,$$

and is therefore an invariant. We take as our fundamental equation of motion the condition of the vanishing of the first variation of the invariant integral

$$\int_{\lambda=\lambda_1}^{\lambda=\lambda_2} L . dJ.$$

This integral may be called the Action of the charged particle along the portion of the historical route which it pervades, defined by the inequalities

$$\lambda_1 \leqslant \lambda \leqslant \lambda_2.$$

From this "principle of least action" we deduce the Lagrangian equations

$$\frac{d}{dJ} \cdot \frac{\partial L}{\partial \dot{x}_\alpha} = \frac{\partial L}{\partial x_\alpha}, \quad \alpha = 1, 2, 3, 4,$$

which are equivalent to the equations of motion given in the preceding section. If

$$\frac{\partial L}{\partial x_\alpha} = 0,$$

x_α is called an "ignorable" coordinate (other coordinates being called "palpable" coordinates), and

$$\frac{\partial L}{\partial \dot{x}_\alpha} = \text{a constan}$$

is an immediate first integral of the equations of motion.

7. We now transform the Lagrangian equations by means of the Legendrian contact-transformation, obtained by writing

$$p_\alpha^{(x)} = \frac{\partial \mathrm{L}}{\partial \dot{x}_\alpha}, \quad \alpha = 1, 2, 3, 4,$$

$$\mathrm{H} = \sum_\alpha p_\alpha^{(x)} \cdot \dot{x}_\alpha - \mathrm{L},$$

when the equations of motion assume the canonical form

$$\frac{\partial \mathrm{H}}{\partial p_\alpha^{(x)}} = \frac{dx_\alpha}{d\mathrm{J}}; \quad \frac{\partial \mathrm{H}}{\partial x_\alpha} = -\frac{dp_\alpha^{(x)}}{d\mathrm{J}};$$

since

$$p_\alpha^{(x)} = m \sum_\beta \mathrm{J}_{\alpha\beta}^{(x)} \cdot \dot{x}_\beta + \frac{e}{c} \mathrm{F}_\alpha^{(x)},$$

we deduce that

$$\sum_\alpha p_\alpha^{(x)} \cdot \dot{x}_\alpha = \mathrm{L} + \frac{m}{2} \Sigma \mathrm{J}_{\alpha\beta}^{(x)} \cdot \dot{x}_\alpha \cdot \dot{x}_\beta$$

and

$$\dot{x}_\beta = \frac{1}{m} \sum_\alpha \mathrm{J}_{(x)}^{\alpha\beta} \cdot p_\alpha^{(x)} - \frac{e}{mc} \sum_\alpha \mathrm{J}_{(x)}^{\alpha\beta} \mathrm{F}_\alpha^{(x)}.$$

Hence

$$\mathrm{H} = \frac{1}{2m} \sum_{\alpha,\beta} \mathrm{J}_{(x)}^{\alpha\beta} \cdot p_\alpha^{(x)} \cdot p_\beta^{(x)} - \frac{e}{mc} \sum_{\alpha,\beta} \mathrm{J}_{(x)}^{\alpha\beta} \cdot p_\alpha^{(x)} \cdot \mathrm{F}_\beta^{(x)} + \frac{e^2}{2mc^2} \sum_{\alpha,\beta} \mathrm{J}_{(x)}^{\alpha\beta} \cdot \mathrm{F}_\alpha^{(x)} \cdot \mathrm{F}_\beta^{(x)}.$$

8. In order to indicate that H is a function of x_α and $p_\alpha^{(x)}$ only, we shall write it in the form

$$\mathrm{H}(x_1, x_2, x_3, x_4 ; p_1, p_2, p_3, p_4).$$

Now

$$\frac{d\mathrm{H}}{d\mathrm{J}} = \sum_\alpha \left(\frac{\partial \mathrm{H}}{\partial x_\alpha} \cdot \frac{dx_\alpha}{d\mathrm{J}} + \frac{\partial \mathrm{H}}{\partial p_\alpha^{(x)}} \cdot \frac{dp_\alpha^{(x)}}{d\mathrm{J}} \right) \equiv 0,$$

$\therefore$ $\mathrm{H} = k$, a constant.

Hence by Jacobi's Theorem, if

$$\mathrm{W}(x_1, x_2, x_3, x_4 ; a_1, a_2, a_3, k) + a_4 = 0$$

be any complete integral of the partial differential equation of the first order and second degree,

$$\mathrm{H}\left(x_1, x_2, x_3, x_4 ; \frac{\partial \mathrm{W}}{\partial x_1}, \frac{\partial \mathrm{W}}{\partial x_2}, \frac{\partial \mathrm{W}}{\partial x_3}, \frac{\partial \mathrm{W}}{\partial x_4} \right) = k,$$

the integrals of the canonical equations of motion are

$$\frac{\partial W}{\partial a_i}=b_i, \quad (i=1, 2, 3), \quad \frac{\partial W}{\partial k}=J-J_0,$$

and

$$\frac{\partial W}{\partial x_i}=p_i^{(x)}, \quad (i=1, 2, 3, 4),$$

where $b_i\,(i=1, 2, 3)$ and J_0 are arbitrary constants.

Planetary Motion.

1. In the preceding exposition of the method of reducing particle dynamics according to the theory of relativity to a system of canonical equations, it has not been necessary to make any hypothesis regarding the actual form of the laws of gravitation and electromagnetism. We shall now discuss the problem of planetary motion according to the first three laws of gravitation mentioned on p. 86 of 'The Principle of Relativity,' by Whitehead, making the usual assumptions that the sun is at rest, and that perturbations due to the attraction of planets other than the one whose motion we consider may be neglected.

2. *Einstein's Law.*

Let $J^{(x)}$ denote the value of the symmetric determinant formed by the components of the fundamental tensor $\|J_{\mu\nu}^{(x)}\|$. Then the ten functions $J_{\mu\nu}^{(x)}$, $(\mu, \nu=1, 2, 3, 4)$ satisfy the ten partial differential equations of the second order,

$$\sum_{\rho}\left[\frac{\partial}{\partial x^{\rho}}J\left[\begin{matrix}\mu\nu\\ \rho\end{matrix}\right]^{(x)}+J\left[\begin{matrix}\mu\nu\\ \rho\end{matrix}\right]^{(x)}\frac{\partial}{\partial x_{\rho}}\log\left\{-J^{(x)}\right\}^{\frac{1}{2}}\right]$$

$$=\sum_{\rho,\sigma}J\left\{\begin{matrix}\mu\sigma\\ \rho\end{matrix}\right\}^{(x)}\cdot J\left\{\begin{matrix}\nu\rho\\ \sigma\end{matrix}\right\}^{(x)}+\frac{\partial^2\log\left\{-J^{(x)}\right\}^{\frac{1}{2}}}{\partial x_{\mu}\cdot\partial x_{\nu}},$$

$$\mu, \nu=1, 2, 3, 4.$$

Since these equations are covariant, if $\|J_{\mu\nu}^{(x)}\|$ is any set of ten functions satisfying them, and

$$x_{\mu}=x_{\mu}(\xi_1, \xi_2, \xi_3, \xi_4), \quad \mu=1, 2, 3, 4$$

is a set of four equations defining a transformation from the system "x" to the system "ξ," then the ten functions

$$J_{\mu\nu}^{(\xi)}=\sum_{\alpha,\beta}J_{\alpha\beta}^{(x)}\frac{\partial x_{\alpha}}{\partial\xi_{\mu}}\cdot\frac{\partial x_{\beta}}{\partial\xi_{\nu}}, \quad \mu, \nu=1, 2, 3, 4$$

will also satisfy the equations, if ξ be substituted for x.

To obtain solutions of these equations appropriate to the solar field, many writers have assumed that the fundamental differential invariant of the dynamic manifold associated with the solar field is expressible in the form

$$dJ^2 = \epsilon^{\nu} . c^2 dt^2 - \epsilon^{\lambda} . dr^2 - \epsilon^{\mu} . r^2(d\theta^2 + \sin^2\theta . d\phi^2),$$

where (r, θ, ϕ) are spherical polar spatial coordinates, t is the temporal coordinate, ϵ the base of Napierian logarithms, and λ, μ, ν functions of r only.

Thus the following writers have obtained solutions satisfying the above hypothesis and the supplementary conditions

$$\operatorname*{Lt}_{r\to\infty} (\lambda, \mu, \nu) = 0$$

together with other simplifying assumptions:—Einstein (4), $[\lambda + 2\mu + \nu = 0,\ i.e.\ J = -c^2 r^4 \sin^2\theta]$; Dröste (6), $[\lambda = 0]$; Schwarzschild (5), $[\mu = 0]$; de Sitter, Hill and Jeffery (7) and (8), $[\lambda = \mu]$. Combridge (9) has shown that the general solution of Einstein's equations, subject to the condition that dJ^2 is expressible in the above form, may be written

$$\epsilon^{\lambda} = \frac{1}{(1 - 2m/f)} \cdot \left(\frac{df}{dr}\right)^2, \quad \epsilon^{\mu} = \frac{f^2}{r^2}, \quad e^{\nu} = 1 - \frac{2m}{f},$$

where f is an arbitrary function of r, and m a constant of integration. To satisfy the supplementary conditions, we must have

$$\operatorname*{Lt}_{r\to\infty} f = r \quad \text{and} \quad \operatorname*{Lt}_{r\to\infty} \left(\frac{df}{dr}\right) = 1.$$

Finally, Forsyth (10) has shown that if dJ^2 is expressible in the form

$$a . dr^2 + b d\theta^2 + c d\phi^2 + d . dt^2,$$

where a, b, c, d are functions of r, θ, ϕ only, and

$$\operatorname*{Lt}_{r\to\infty} (a, b, c, d) = (-1, -r^2, -r^2 \sin^2\theta, c^2),$$

then we reach once more the solution

$$dJ^2 = \left(1 - \frac{2m}{r}\right) c^2 dt^2 - \frac{1}{\left(1 - \frac{2m}{r}\right)} dr^2 - r^2(d\theta^2 + \sin^2\theta . d\phi^2).$$

m is called the "gravitational radius" of the sun and equals $\frac{\gamma M}{c^2}$, where

γ = the constant of gravitation,
M = the mass of the sun,
c = the velocity of light *in vacuo* where the gravitational field is zero.

The Lagrangian function is

$$L=\tfrac{1}{2}\mu\left[\left(1-\frac{2m}{r}\right)c^2\dot{t}^2-\frac{\dot{r}^2}{\left(1-\frac{2m}{r}\right)}-r^2\dot{\theta}^2-r^2\sin^2\theta\,.\,\dot{\phi}^2\right].$$

The ignorable coordinates ϕ and t yield the equations

$$\mu r^2\sin^2\theta\,.\,\dot{\phi}+p_\phi=0,$$

$$\mu c^2\left(1-\frac{2m}{r}\right)\dot{t}=p_t,$$

where p_θ, p_ϕ, p_t are constants.

Let the axes be oriented so that $p_\phi=0$. Then $\mu r^2\dot{\theta}+p_\theta=0$. Then the Hamiltonian equation is

$$\frac{1}{\left(1-\frac{2m}{r}\right)c^2}\left(\frac{\partial W}{\partial t}\right)^2+\left(1-\frac{2m}{r}\right)\left(\frac{\partial W}{\partial r}\right)^2-\frac{1}{r^2}\left(\frac{\partial W}{\partial\theta}\right)^2=\eta,$$

and this possesses a complete integral in the form

$$W=p_\theta\,.\,\theta+p_t\,.\,t+z,$$

where z is a function of r only.

Put $r\,.\,u=1$, and we obtain the differential equation

$$u^4(1-2m\,.\,u)\left(\frac{dz}{du}\right)^2=p_\theta{}^2\,.\,U,$$

where
$$U=2mu^3-u^2+\frac{2m\eta}{p_\theta{}^2}\,.\,u+\frac{p_t{}^2-\eta c^2}{p_\theta{}^2c^2}\,.$$

Hence
$$z=\pm\int\frac{p_\theta\,.\,U^{\frac{1}{2}}\,.\,du}{u^2(1-2mu)}$$

and
$$\frac{\partial W}{\partial p_\theta}=\theta+\frac{\partial z}{\partial p_\theta}=\theta\pm\int\frac{du}{U^{\frac{1}{2}}}.$$

Since $\eta=\mu^2$, this is the elliptic integral discussed by Forsyth (11).

Let
$$U=2m(u-\alpha)(u-\beta)(u-\gamma),$$

where
$$\gamma\leq u\leq\beta<\alpha.$$

Then, it is shown in Forsyth's paper that α, β, γ, the roots of the equation $U=0$, are real, distinct, and positive in the solar field.

Let $$p^2=2\mu(\alpha-\gamma)=\frac{\alpha-\gamma}{\alpha+\beta+\gamma}.$$

Measuring θ from aphelion ($u=\gamma$), we have, as in Greenhill's paper (12),

$$\sqrt{\frac{u-\gamma}{\beta-\gamma}}=\mathrm{sn}\frac{p\theta}{2}\left(\mathrm{mod}\sqrt{\frac{\beta-\gamma}{\alpha-\gamma}}\right),$$

where sn is Jacobi's elliptic function defined by the equations

$$y=\int_0^x\frac{dx}{\sqrt{(1-x^2).(1-\kappa^2x^2)}},\qquad |\kappa|<1,$$
$$x=\mathrm{sn}\,y\pmod{\kappa}.$$

A discussion of the possible forms of the orbit has been given by Morton (13).

Let K denote the first complete elliptic integral modulus $\sqrt{\frac{\beta-\gamma}{\alpha-\gamma}}$, *i. e.* the real quarter period of sn y, then the perihelionic advance in radians per revolution is

$$\psi=\frac{4\mathrm{K}}{p}-2\pi.$$

For all the inner planets this is approximately $6\pi\frac{m^2}{h^2}$, where $\mu h+p_\theta=0$. With the usual notation

a = semi-axis major

and e = eccentricity of orbit.

By Forsyth's analysis $h^2\sim ma(1-e^2)$, hence

$$\psi\sim\frac{6\pi\gamma\mathrm{M}}{c^2a(1-e^2)}.$$

3. *Whitehead's First Law.*

For the solar field this law can be expressed in the integral form

$$d\mathrm{J}^2=(c^2dt^2-dr^2-r^2d\theta^2-r^2\sin^2\theta\,.\,d\phi^2)-\frac{2\gamma\mathrm{M}}{c^2r}(c^2dp^2),$$

where $$c(dt-dp)=dr,$$

whence the Lagrangian function is

$$\mathrm{L}=\tfrac{1}{2}\mu\left[\left(1-\frac{2m}{r}\right)c^2\dot{t}^2-\left(1+\frac{2m}{r}\right)\dot{r}^2-r^2\dot{\theta}^2-r^2\sin^2\theta\,.\,\dot{\phi}^2+\frac{4mc}{r}r\dot{t}\right].$$

The Lagrangian equations for the ignorable coordinates ϕ, γ are

$$\left.\begin{aligned} \mu r^2 \sin^2\theta\dot{\phi}+p_\phi&=0,\\ \mu\left(1-\frac{2m}{r}\right)c^2\dot{t}+\mu\frac{2mc}{r}\dot{r}&=p_t,\end{aligned}\right\}$$

where p_ϕ and p_t are constants.

Choosing axes so that $p_\phi=0$, we find that the Hamiltonian equation is

$$\frac{1}{c^2}\left(1+\frac{2m}{r}\right)\left(\frac{\partial W}{\partial t}\right)^2-\left(1-\frac{2m}{r}\right).\left(\frac{\partial W}{\partial r}\right)^2-\frac{1}{r^2}\left(\frac{\partial W}{\partial\theta}\right)^2 + \frac{4m}{rc}\left(\frac{\partial W}{\partial r}\right)\left(\frac{\partial W}{\partial t}\right)=\eta,$$

and $$\mu r^2\dot{\theta}+p_\theta=0,$$

and this possesses a complete integral in the form

$$W=p_\theta.\theta+p_t.t+z,$$

where z is a function of r only.

Putting $r.u=1$, we obtain the equation

$$K\left(\frac{dz}{du}\right)^2+2L\left(\frac{dz}{du}\right)+M=0,$$

where $$K=(1-2mu)u^4\ ;\quad L=2m\frac{p_t}{c}u^3\ ;$$

$$M=\left(p_\theta{}^2u^2-2m\frac{p_t{}^2}{c^2}-\frac{p_t{}^2}{c^2}+\eta\right).$$

Hence $$\frac{dz}{du}=\frac{\frac{2mp_tu^3}{c}\pm p_\theta{}^2u^2U^{\frac{1}{2}}}{(1-2mu)u^4},$$

where $$U=2mu^3-u^2+\frac{2m\eta}{p_\theta{}^2}u+\frac{p_t{}^2-\eta c^2}{p_\theta{}^2c^2},$$

the same cubic as that which occurred in the previous paragraph ;

$$\therefore\quad z=\int\frac{2mp_tdu}{(1-2mu)cu}\pm\int\frac{p_\theta.U^{\frac{1}{2}}.du}{(1-2mu)u^2}$$

and $$\frac{\partial W}{\partial p_\theta}=\theta+\frac{\partial z}{\partial p_\theta}=\theta\pm\int\frac{du}{U^{\frac{1}{2}}}.$$

Hence we regain exactly the same equation to the form of the orbit as in the previous paragraph.

4. *Whitehead's Second Law.*

In rectangular Cartesian axes this law may be written

$$\sum_{\lambda} \frac{1}{\omega_\lambda{}^2} \frac{\partial}{\partial x_\lambda} \mathrm{J} \left[{\mu\nu \atop \lambda} \right]^{(x)} = 0, \quad \mu, \nu = 1, 2, 3, 4,$$

where the constants ω_λ are those which occur in the expression for the linear element of the metric manifold

$$ds^2 = \sum_{\lambda} \omega_\lambda{}^2 dx_\lambda{}^2.$$

Up to the present no researches on the equations have been published. We shall consider only those solutions which correspond to a steady gravitational field, *i. e.* for which $\mathrm{J}_{\mu\nu}^{(x)}$ is independent of x_4.

By writing $\mu = \nu = 4$, we obtain the equation

$$\frac{\partial^2 \mathrm{J}_{44}^{(x)}}{\partial x_1{}^2} + \frac{\partial^2 \mathrm{J}_{44}^{(x)}}{\partial x_2{}^2} + \frac{\partial^2 \mathrm{J}_{44}^{(x)}}{\partial x_3{}^2} = 0.$$

The general solution of this equation, subject to the condition that $\mathrm{J}_{44}^{(x)}$ is a function of r only where

$$r = \sqrt{x_1{}^2 + x_2{}^2 + x_3{}^2},$$

is

$$\mathrm{J}_{44}^{(x)} = c^2 \left(1 - \frac{2m}{r} \right),$$

c, m being constants of integration.

Assume that in spherical polar coordinates (r, θ, ϕ), $d\mathrm{J}^2$ can be expressed in the form

$$d\mathrm{J}^2 = \left(1 - \frac{2m}{r} \right) c^2 dt^2 - (1 + f(r) . r^2) dr^2 - r^2 d\theta^2 - r^2 \sin^2 \theta . d\phi^2 - g(r) r \, dr \, dt,$$

where $f(r)$ and $g(r)$ are functions of r only.

Then

$$\mathrm{J}_{\mu\mu}^{(x)} = -1 - x_\mu{}^2 . f(r), \qquad \mu \neq 4,$$

$$\mathrm{J}_{\mu\nu}^{(x)} = -x_\mu x_\nu . f(r), \quad \mu \neq \nu \, ; \; \mu, \nu \neq 4,$$

$$\mathrm{J}_{\mu 4}^{(x)} = -x_\mu . g(r), \qquad \mu \neq 4.$$

The ten equations which express Whitehead's Second Law

may be divided into three groups, obtained by setting

$$(1)\ \mu, \nu \neq 4, \qquad \mu = \nu;$$
$$(2)\ \mu, \nu \neq 4, \qquad \mu \neq \nu;$$
$$(3)\ \nu = 4, \qquad \mu \neq 4.$$

The necessary and sufficient conditions for the satisfaction of groups (1) and (2) are respectively the equations

$$3f(r) + r\frac{df}{dr} = 0$$

and

$$5\frac{df}{dr} + r\frac{d^2f}{dr^2} = 0.$$

Hence $f(r)$ reduces to a constant λ.

The third group of equations is satisfied identically, whatever the form of the function $g(r)$.

In order that the expression for dJ^2 in polar coordinates should tend towards the form

$$c^2dt^2 - dr^2 - r^2d\theta^2 - r^2\sin^2\theta \,.\, d\phi^2$$

as r tends to infinity, λ must be zero, and $\operatorname{Lt}_{r\to\infty} g(r)$ must be of higher order than $\frac{1}{r}$.

Let $$r \,.\, g(r) = \mathrm{R}(r).$$

Taking as our expression for dJ^2

$$\left(1 - \frac{2m}{r}\right)c^2dt^2 - dr^2 - r^2d\theta^2 - r^2\sin^2\theta \,.\, d\phi^2 - \mathrm{R}(r)dr\,dt,$$

we find as the Lagrangian function

$$\mathrm{L} = \frac{1}{2}\mu\left[\left(1 - \frac{2m}{r}\right)c^2\dot{t}^2 - \dot{r}^2 - r^2\dot{\theta}^2 - r^2\sin^2\theta \,.\, \dot{\phi}^2 - \mathrm{R}\dot{r}\dot{t}\right].$$

The Lagrangian equations for the ignorable coordinates r, ϕ are

$$\mu r^2\sin^2\theta \,.\, \dot{\phi} + p_\phi = 0,$$

$$\mu\left(1 - \frac{2m}{r}\right)c^2\dot{t} - \frac{1}{2}\mu\mathrm{R}\dot{r} = p_t,$$

where p_ϕ and p_t are constants.

When the axes are oriented so that $p_\phi = 0$, the Hamiltonian equation is

$$\frac{1}{(4\lambda + R^2)}\left\{2\left(\frac{\partial W}{\partial t}\right)^2 - 2\lambda\left(\frac{\partial W}{\partial r}\right)^2 - 2R\left(\frac{\partial W}{\partial r}\right)\left(\frac{\partial W}{\partial t}\right)\right\} - \frac{1}{r^2}\left(\frac{\partial W}{\partial \theta}\right)^2 = \eta,$$

and $$\mu r^2\dot{\theta} + p_\theta = 0,$$

where $$\lambda = c^2\left(1 - \frac{2m}{r}\right).$$

This possesses a complete integral in the form

$$W = p_\theta . \theta + p_t . t + z,$$

where z is a function of r only.

Put $r . u = 1$, and we obtain the equation

$$K\left(\frac{dz}{du}\right)^2 + 2L\left(\frac{dz}{du}\right) + M = 0,$$

where $$K = -2\lambda u^4,$$

$$L = R . p_t . u^2,$$

and $$M = 2p_t^2 - (2\lambda + \tfrac{1}{2}R^2)(p_\theta^2 . u^2 + \eta).$$

Hence $$\frac{dz}{du} = \frac{-Rp_t \pm c\sqrt{Q}}{-2\lambda u^2},$$

where $$Q = 4p_\theta^2 . c^2\left(2mu^3 - u^2 - \frac{2m\eta}{p_\theta^2}u + \frac{p_t^2 - \eta c^2}{p_\theta^2 c^2}\right)\left(1 - 2mu + \frac{R^2}{4c^2}\right).$$

Proceeding as before, we find that

$$\theta = \pm\int \frac{2c\left(1 - 2mu + \frac{R^2}{4c^2}\right)}{\sqrt{Q}}\, du.$$

Hence the necessary and sufficient condition that this should reduce to the same relation between u and θ as that obtained in the two theories just discussed, is that

$$R = 2c\sqrt{2mu}.$$

This leads to $$g(r) = \frac{2c\sqrt{2m}}{r^{3/2}},$$

and hence satisfies the supplementary conditions, respecting the form of dJ^2 as r tends to infinity.

Deviation of Light Rays as in the Solar Field.

It is shown in Murnaghan's paper (1) that the equations to the paths of rays of light in the solar field may be obtained by writing

$$\frac{1}{p_\theta}, \frac{1}{p_t} \to 0,$$

$$\frac{p_t}{p_\theta} \to \text{a finite quantity.}$$

The cubic U then takes the form

$$2mu^3 - u^2 - \alpha^2,$$

and in the practical application of the analysis to the solar field the three roots u_1, u_2, and u_3 of the equation $U = 0$ are real, distinct, and satisfy the inequalities

$$u_1 < 0 \leqslant u \leqslant u_2 < u_3.$$

Hence, if $$\frac{u - u_1}{u_2 - u_1} = \sin^2 . \psi$$

and $$\kappa^2 = \frac{u_2 - u_1}{u_3 - u_1},$$

the equation to the path of a ray of light on all three theories is

$$\theta = \int_0^u \frac{du}{U^{1/2}} = \sqrt{\frac{2}{m(u_3 - u_1)}} \int_{\sin^{-1}\sqrt{\frac{u_1}{u_1 - u_3}}}^{\psi} \frac{d\psi}{\sqrt{1 - \kappa^2 \sin^2 \psi}},$$

whence the approximate value of the total angular deviation suffered by a ray whose minimum distance from the sun is $\frac{1}{u_2}$ is found to be $4mu_2$ radians.

Conclusion.

It will be seen that the preceding method of treating the problem of central orbits according to relativistic theories has two merits to recommend it to the computor—it evades the tedious calculation of the Christoffel 3-index symbols, and it focusses attention at once on a differential equation, the solution of which furnishes the key to the whole problem. The principal results established in this paper by the use of this method are the following :—

(1) The equation of a planetary orbit has precisely the same form on Einstein's theory as on Whitehead's first

theory. In Whitehead's book, 'The Principle of Relativity,' it was shown that both theories yield the same expression for the perihelionic advance to a first approximation. This paper shows the exact equivalence of the formulæ.

(2) The equation of a planetary orbit on Whitehead's second theory involves an arbitrary function which can be chosen to yield the same equation as in the previous cases. This second theory has not been studied before.

Thus no observations of the forms of planetary orbit can discriminate between these three theories.

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XXXII. *Radioactive Disintegration Series.*—Part II.* *By* W. P. Widdowson, *B.A., Scholar of Christ Church, Oxford, and* A. S. Russell, *M.A., D.Sc., Dr. Lee's Reader in Chemistry* †.

§ 1. *Introduction.*

In Part I. it was shown that radioactive disintegration series are limited to four in number, the members of which have atomic weights given respectively by $4n+3$, $4n+2$, $4n+1$, and $4n$, where n is an integer. Reasons were given for supposing that the first of these is the actinium series, the second the uranium series, the third a hypothetical series the end-products of which may be isotopes of bismuth ($a=209$) and of thallium ($a=205$), and the fourth the thorium series. The present paper deals with the hypothetical series. It will show that experimental evidence is against the existence of this series in the possible form given in the earlier paper, and that theoretical considerations are not only consistent with this view, but render the existence of the series in any but an attenuated form unlikely.

§ 2. *Method of Investigation.*

The hypothetical series as postulated has a gaseous member of atomic number (z) 86 and of atomic weight (a) 221, which will for convenience be referred to as X. As an electroscope can detect a much smaller amount of a gaseous radio-element than of a solid one, this member of the series appears to be the most suitable for examination. Its expected period, also, is a convenient one. This may be calculated from the periods of radon and thoron by the relation given in the paper cited, namely that the periods of radon, of X the hypothetical member considered, of thoron, and of acton are roughly in the ratio of $80^3 : 80^2 : 80 : 1$. An eightieth of radon's period is 69·3 minutes; eighty times thoron's is 72·0 minutes; the mean value of X's expected period is consequently 70·6 minutes. If this series existed along with the radium series in uranium minerals in such an amount that, for every hundred radon atoms breaking up per second, one or more atoms of X break up, then it is likely that the

* Part I., A. S. Russell, Phil. Mag. xlvi. p. 642 (1923).

† Communicated by the Authors.

series would have long ago been detected in the ordinary course of experiment. But if the equilibrium ratio were less than one per cent., X probably would not have been detected unless it had been specially looked for. It is clear, however, that if X exists and has a period of about an hour, its detection, even when the equilibrium ratio is as low as 1 to 1000, should not be very difficult. For if X and radon be completely removed from the mineral and then allowed to accumulate for an hour, the ratio of their relative activities is raised from $\frac{1}{1000}$ to $\frac{1}{5}$ because of the difference in their periods. If emanation of this composition be examined in an electroscope, it would be expected to show different properties from those of the two emanations in the proportions in which they naturally occur. It is quite possible, however, that X might exist and not have a period of the expected value. The closer the period is to that of radon the more difficult it would be to detect it. But if the period were much longer than that of radon it might easily have been overlooked, although, if it were looked for, it should be possible to detect it. Shortness of period would make detection easier provided the period is not so short that X has decayed considerably in the time of its transference from its parent-substance to the electroscope. The expulsion of β-particles instead of α-particles by X would, other things being the same, make the detection of X much more difficult.

Failure to detect X may, then, be ascribed to one of four principal reasons :—

(1) The parent of X may exist, but not in any of the preparations investigated.

(2) X may exist in measurable amount, but its period is such that it is not likely to be detected without elaborate precautions.

(3) X may have a suitable period and exist in uranium minerals, but in so small a proportion that in the unavoidable presence of radon it cannot be detected by ordinary means.

(4) X does not exist.

In the present investigation we have looked for X only in the minerals pitchblende and thorianite and in a preparation of radium separated from pitchblende a few years ago. The first two of these are likely sources. Further, we have done only such experiments as are likely to reveal X if its period lies between four hours and four minutes.

§ 3. *Experimental work.*

4 grams of a pitchblende containing 25 per cent. U_3O_8 was dissolved in nitric acid, 3·5 grams of barium chloride added, and the barium containing radium and the parent of X (an isotope of radium, if it exists) removed as sulphate. The sulphate was converted into barium carbonate by fusing with fusion mixture, and the carbonate dissolved in dilute hydrochloric acid to give a clear solution. When this solution is boiled the emanation is quantitatively expelled, as is well known. In the experiments to be described it is essential that this occurs, for otherwise the alteration in the ratio of the amounts of radon and of X by their growth for a known period of time after supposed complete expulsion, would not be that calculated from their known or supposed periods. In all experiments the emanation was transferred without loss through a drying apparatus to an air-tight emanation electroscope. Experiments to test if the emanation could be completely removed from the solutions used, and if the emanation electroscope was working properly, led to the following satisfactory results :—

Radium solution from pitchblende containing 25·4 per cent. U_3O_8. 1 scale-division of the instrument corresponds to 9·6, 9·5, 9·3, 9·5, and $9·6 \times 10^{-8}$ mg. radium in different experiments.

Radium solution from thorianite containing 35·8 per cent. U_3O_8. 1 scale-division of the instrument corresponds to 9·5 and $9·5 \times 10^{-8}$ mg. radium in two experiments.

Experiment I.—The solution of barium-radium chloride from pitchblende was made up to 45 c.c. 3 c.c. of this was placed in a flask, diluted with water, and the emanation expelled. A quarter of an hour later this operation was repeated. The flask was then sealed up for 2 days. At the end of this time the emanation was completely expelled into a gas-holder, and a few minutes later transferred to the electroscope through a tube containing calcium chloride to dry the gas, and through another to remove, as far as possible, solid disintegration products in the gas. Readings of the ionization produced in the electroscope were taken continuously every few minutes for three hours and then at longer intervals for the next hour. The maximum value, obtained by taking the mean of those obtained between $2\frac{1}{2}$ and 3 hours after the transfer of the emanation into the electroscope, was taken as 100, and all values calculated on

this basis. A continuous curve was obtained when the values were plotted against the time. Four experiments of this kind were carried out. The mean values from the closely-agreeing curves at intervals of five and ten minutes are given in the column under I. in Table I.

TABLE I.

Time in minutes.	Pitchblende.				Radium.	Thorianite.
	I. Growth 2 days.	II. Growth 2½ hours.	III. Growth 30 mins.	IV. Growth 1 min.	V. Growth 1 min.	VI. Growth 2 mins.
5	59·8	62·6	62·8	68·0	68·5	—
10	65·4	68·4	68·8	71·0	71·0	70·6
15	69·4	71·8	71·8			
20	72·2	74·0	74·0	76·0	76·0	74·2
25	74·6	76·2	75·8			
30	76·8	78·2	77·6	79·0	79·5	77·5
35	79·0	79 8	79·4			
40	81·0	81·2	81·0	82·0	82·4	81·0
45	82·4	82·6	82·4			
50	84·0	84·0	83·8	84·8	85·4	84·0
55	85·4	85·4	85·2			
60	86·8	86·8	86·6	87·6	88·0	87·0
70	89·2	89 4	89·0			
80	91·6	91·6	91·0	92·4	92·4	91·2
90	93·8	93·6	93·0			
100	95·4	95·2	94·8	96·3	96·0	95·2
110	96·6	96·8	96·4			
120	97·8	97·8	97·8	98	98	98
130	98 6	98·8	98·4			
140	99·2	99·2	99·2	99	99	99·5
150	99·7	99·6	99·4			
160	100	100	100	100	100	100

Experiment II.—42 c.c. of the solution used in experiment I. were placed in a flask and the emanation completely expelled. This operation was repeated, and the flask was then sealed up for 2½ hours. At the end of this time the emanation was removed, as before, from the flask into the electroscope. Measurements were made as in experiment I. Five experiments were carried out. The mean values of the relative ionizations produced are given in the column under II. in Table I.

Experiment III.—A solution of barium-radium chloride was separated from such a quantity of pitchblende that the quantity of radon which grew in it in half-an-hour gave an ionization in the electroscope that could be conveniently measured. The emanation was completely expelled, the flask sealed up for 30 minutes, and at the end of this time

the emanation which had grown was removed to the electroscope. Measurements were made as in experiments I. and II. Four experiments were carried out. The mean values of the relative ionizations produced are given in the column under III. in Table I.

Experiment IV.—This was carried out in a similar way, but on a much larger quantity of active material. The emanation was allowed to grow, after complete expulsion, for 1 minute only and then drawn directly into the evacuated electroscope. Three experiments were carried out. The mean values of the relative ionizations produced are given in the column under IV. in Table I.

Experiment V.—This experiment was carried out like experiment IV. on a solution of radium which had been extracted from pitchblende a few years ago. Six experiments were made.

Experiment VI.—This was carried out on a solution of barium-radium-mesothorium chloride extracted by us from a specimen of thorianite containing 35·8 per cent. U_3O_8 and about 55 per cent. ThO_2 in the following way:—The emanations were completely expelled. They were then allowed to grow for two minutes, at the end of which time they were removed to a gas-holder and kept there for 7 minutes to allow the thoron to decay to $\frac{1}{250}$ of its initial value, and then drawn into the evacuated electroscope. The first measurements were not accurate because the ionization was too great. Ten minutes after the transfer the effect of the thoron was negligible, and measurements thereafter were continued as before. Three experiments were carried out, the results of which are given in Table I. under VI.

§ 4. *Discussion of Results.*

The results in the table may be divided into two groups: those in columns I. II. III. and VI., and those in columns IV. and V. It is seen that the results in the first three columns are very similar from 40 minutes to 160 minutes, but that the earlier values of I. are slightly smaller than the corresponding values of II. and III., which are very similar. If this difference is genuine it seems to be explained best by saying that X has a period of about 15 minutes and constitutes about 5 per cent. of the activity of radon and its products after they are five minutes in the electroscope under the conditions of experiments II. and III. This, however, leads to difficulties. For if the ratio of the

activities of radon and of X in pitchblende is 1000, then, in experiment I., it may be calculated to be 302, and so X would be presumed undetectable. In experiment II. the ratio would be 18·6, which is approximately the ratio apparently detected. But in experiment III. the ratio would be as low as 5, and so X would contribute nearly four times more ionization than is found experimentally. In other words, the presence of a short-lived emanation would explain the differences between I. and II. but not the similarities of II. and III. On the other hand, the similarities would be consistent with the presence of an emanation with a period of 3 hours or more, but this product would not explain the differences between I. and II., which disappear after about 40 minutes. The difficulty cannot be resolved by considering in addition to X its possible active deposit, for although the nature and amount of the active deposit would be different in I., II., and III. in the emanations before they were transferred to the electroscope, this difference can hardly be operative inside the electroscope as the greater part of the deposit is prevented from entering by the glass wool and the drying agent. The difference under discussion is about three times the estimated experimental error.

The results of columns IV. and V. closely agree, but differ from those of the other columns. It would appear that a one-minute growth reveals something which the other experiments do not. The difference, we think, can best be explained as follows:—In experiments IV. and V. the emanation was transferred directly and in a few seconds from the vessel where it had grown to the electroscope. In experiments I., II., and III. the emanation was first collected in a gas-holder over water and then transferred to the electroscope, an operation taking about ten minutes. The effect of this difference in operations seems to make a difference of about six minutes to the times at which corresponding amounts of active deposit are formed in the emanation; the curves we obtained in IV. and V. are unmistakably those of II. and III. except for a shift of the time-axis by about six minutes. This may be seen also from Table I. If five minutes be added to the times given for the results of IV. and V., then the ionizations in II., III., IV. and V. are approximately the same.

An alternative explanation is that the effect is genuine and due to X. If so, X has an initial value of about 6 units, which falls to 2 in five minutes, to $1\frac{1}{2}$ in fifteen minutes, and remains 1 till a hundred minutes. It is

therefore at least two products, one with a period of about three minutes and the second of two or three hours or so. The former product, if just detectable in an experiment in which the emanation accumulated for one minute, would not be detectable in experiments I., II., and III., so that the experimental results are consistent with the existence of this body.

Experiment IV. was again carried out with this difference, that the transfer of emanation was made as in experiments I., II., and III.; the results were approximately the same as those of I., II., and III. This is what would be expected on the first of the explanations offered; and also on the second, since during the ten minutes of the transfer the quick-changing emanation has decayed almost to zero, and the second product, presumed not a gas, is prevented from entering the electroscope.

Against the alternative explanation is this: that the ratio of parent and product in α-particle activity cannot be lower than the reciprocal of the ratio of their periods. In this case the former ratio is, at most, 6 and the latter, at least, 20. This objection does not apply if the parent (in this case X) expels a β-particle, and its product an α-particle.

To help to decide the matter experiment II. was repeated, except that on this occasion the accumulated emanation was transferred directly and quickly to the electroscope, as it had been in experiments IV. and V. The results now obtained were those of IV. and V. This shows conclusively that the difference effect is not due to an unknown radioactive body as suggested in the alternative explanation. It is probably due to the fact that in this method of transference a larger proportion of the active deposit of radon evaded the glass-wool and drying-apparatus and accompanied the radon into the electroscope than in the other method. Given a uniform method of transferring the emanation, exact timing of the moment the emanation reaches the electroscope, and a uniform method of measuring the ionization, we think the accuracy of our measurements is about 1 part in 200 when the mean of three values is taken.

In the experiments on the radium containing mesothorium separated from thorianite—experiment VI.—the effect of the thoron was enormous. Even after it had stood for seven minutes after its removal from its parent before being passed into the electroscope it was impossible to measure the combined emanations in the first five minutes. An emanation with a period of few minutes could not

therefore be detected in a source of thorium. In experiment VI., however, when the effect of thoron was spent, the rise-curve obtained was very similar to those obtained in experiments I., II., and III.

It seems, therefore, from these results that the six experiments appear to reveal no effects that cannot be explained without postulating the existence of a body X. They do not, however, exclude the possibilities that X might exist and have a period of the order of a minute, or that it might have a longer period and expel β-particles. It remains to discuss below what fraction of radon its concentration must be for it to exist and yet remain undetected in our experiments.

This fraction is obviously a function of X's supposed period, of the nature and intensity of X's radiation, and of the nature of X's active deposit. We propose to confine ourselves to cases in which it is supposed that X expels α-particles of approximately the range of those from radon, that its period is between 4 minutes and 4 hours, and that the presence of an active deposit neither hinders nor helps the detection of X.

TABLE II.

Supposed period of X, in minutes.	Ionization due to X.	Ratio $\frac{X}{\text{Radon}}$ in		
		Exp. II. Growth $2\frac{1}{2}$ hours.	Exp. III. Growth 30 mins.	Exp. IV. Growth 1 min.
240	10	$\frac{1}{113}$	$\frac{1}{133}$	$\frac{1}{140}$
120	10	$\frac{1}{150}$	$\frac{1}{254}$	$\frac{1}{274}$
60	10	$\frac{1}{264}$	$\frac{1}{469}$	$\frac{1}{551}$
30	12	$\frac{1}{260}$	$\frac{1}{666}$	$\frac{1}{912}$
15	16	$\frac{1}{200}$	$\frac{1}{750}$	$\frac{1}{1350}$
15	10	—	—	$\frac{1}{2160}$
8	15	—	—	$\frac{1}{2600}$
4	20	—	—	$\frac{1}{2350}$

The information, calculated from our results, is given in Table II. In the first column are given various supposed

values of the period of X; in the second, values of ionizations contributed by X which would be detected from our results; and in the third, fourth, and fifth columns, the ratios of the activities of X to radon in a mineral which, in experiments II., III., and IV. respectively, would give the ionizations of column II. The ionizations of column II. are calculated taking the maximum point of radon's rise-curve as 100.

§ 5. *Theoretical Considerations.*

It has been pointed out by one of us* that there is a close relation between the isotopes of radioactive elements and those of the inactive elements, it being possible to deduce in many cases the complexity of the latter from knowledge of the former. We propose here to discuss a converse problem: what light may be thrown on the possibility of the hypothetical series by present knowledge of inactive isotopes?

It may be deduced from Aston's collected results† that if an even element (*i. e.* an element of even atomic number) has an odd isotope (*i. e.* an isotope of odd mass-number), the latter is 3 or 1 units less than the principal even isotope. Indeed the rule seems to be, except for krypton, that when the element has two odd isotopes they are 3 and 1 units less, and when one isotope only, it is 3 units less. Neither of these rules applies to the light elements below sulphur.

Some results in illustration are given in Table III.

Table III.

Element.	Principal even isotope.	Odd isotopes.	
80. Mercury	202§	199	—
54. Xenon	132	129	131
50. Tin	120	117	119
36. Krypton	84	—	83
34. Selenium	80	77	—

§ The likeliest value from Aston's results and atomic weight evidence.

It may also be deduced from Aston's results and from some (denoted by asterisks) given in the former of the papers by one of us cited, that one of the isotopes of an odd element is *usually* 5 units less than the principal even isotope of the element above it, if the latter be

* A. S. Russell, 'Nature,' cxii. p. 588 (1923); Phil. Mag. xlvii. p. 1121 (1924).

† F. W. Aston, Phil. Mag. xlv. p. 934 (1923).

complex, and 1 or 3 units less, if it be simple. (A "simple" even element is one consisting *predominantly* of one isotope.) The rule is not absolute, but the number of exceptions are small and confined to the lighter elements.

Examples in illustration are given in Table IV.

TABLE IV.

Element z.	Nature.	Principal even isotope.	Element $z-1$.	Mass-number.
82. Lead	Complex.	208†	81. Thallium	203*
80. Mercury	,,	202	79. Gold	197*
54. Xenon	,,	132	53. Iodine	127
50. Tin	,,	120	49. Indium	115
36. Krypton	,,	84	35. Bromine	79
34. Selenium	,,	80	33. Arsenic	75
58. Cerium	Simple.	140*	57. Lanthanum	139*
42. Molybdenum	,,	96*	41. Niobium	93*
38. Strontium	,,	88	37. Rubidium	85
26. Iron	,,	56	25. Manganese	55
16. Sulphur	,,	32	15. Phosphorus	31

† Assumed. Very complex elements have as a rule principal even isotopes of mass-number $4n$. 208 is also the nearest even number to the atomic weight.

If both these considerations apply to even radio-active elements, we obtain the possibilities given in Table V.

TABLE V.

Element z.	Principal even isotope.	Possible odd isotopes.	Element $z-1$.	Probable odd isotope.	Possible odd isotopes.
92. Uranium	238	235, 237	91. Protoactinium	233	231, 235
90. Thorium	232	229, 231	89. Actinium	227	225, 229
88. Radium	226	223, 225	87. ——	221	219, 223
86. Radon	222	219, 221	85. ——	217	215, 219
84. Polonium	210	207, 209	83. Bismuth	205	203, 207
82. Lead	208	205, 207	81. Thallium	203	201, 205

The figures in columns 3 and 5 are derived from those in column 2 from the considerations above, and those in column 6 from those in column 5, because an odd element may have two odd isotopes which differ by two units.

In compiling column 5 a difficulty has been to decide which of the even radio-elements are to be treated as complex, and which simple. Regarded as inactive elements, all but lead and possibly uranium are simple: regarded as radioactive elements, they are all complex. We have decided to assume in the first instance that each is complex.

The number of possibilities may now be reduced considerably by making the two following limiting assumptions:—

(1) Uranium is expected to have one odd isotope ; radon and lead two ; thorium, radium and polonium none *. This excludes 237 from uranium, 229 and 231 from thorium, 223 and 225 from radium, and 207 and 209 from polonium as "probable" isotopes. (If they are "possible" they are likely relatively short-lived products.)

(2) Isobares of odd mass-number expelling the same type of radiation do not exist. (No odd isobares have yet been discovered among the inactive elements.)

This excludes 235 from protoactinium, 225 from radon, 219 from elements 87 and 85, 203, 205 and 207 from bismuth, and 205 from thallium. It also implies that successive radioactive changes in series of odd atomic number are confined to a succession of α-particles and to the succession α, β, α, β.

The modified possibilities are given in Table VI. Since bismuth may not have isotopes of 203, 205 and 207 †, it is given the value 209, which is, of course, the experimental value and that to be expected if polonium be regarded as a simple element. If bismuth has a second isotope, it can only be 211. These values are consequently added to the table under "probable" and "possible" respectively.

TABLE VI.

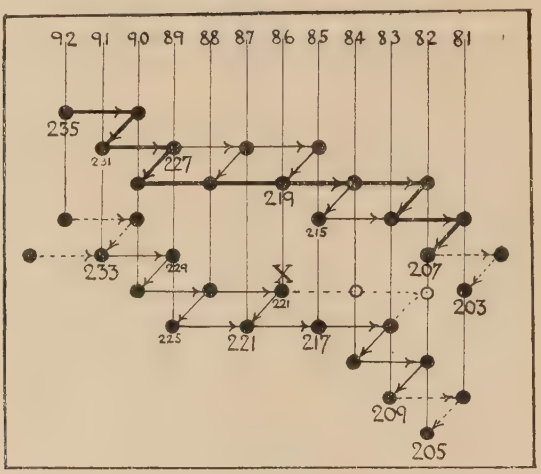
Element z.	Probable odd isotopes.	Possible odd isotopes.
92. Uranium	235	—
91. Protoactinium ...	233	231
90. Thorium	—	—
89. Actinium	227	225 or 229
88. Radium	—	—
87. ——	221	—
86. Radon	219	—
85. ——	217	215
84. Polonium	—	—
83. Bismuth.....	209	211
82. Lead	205. 207	—
81. Thallium	203	—

If it be assumed that elements having mass-numbers greater than 209 are radioactive, two disintegration series

* A. S. Russell, 'Nature,' cxii. p. 588 (1923) ; a fuller account is in course of publication.

† These end-products must be classed as α-ray bodies, for if they were β-ray bodies the second assumption would be contravened.

may be drawn to embrace the above values, one embracing mass-numbers of the form $4n+1$, the other those of the form $4n+3$. Neither of these is unique, various possibilities being allowed by the data. Each series is drawn to pass through the "probable" mass-numbers (printed in large type), through the "possible" mass-numbers (printed in smaller type) and through any mass-number which is not inconsistent with the data given in the above table (these are not printed). The series are shown in the figure.



It is seen that one of the possibilities of the upper series is part or the whole of the actinium series * which is the alternative that does not pass through elements 87 and 85. This is shown in thicker type. A second possibility—namely, that which passes from $z=89$, $a=227$ to $z=87$, $a=223$ and rejoins the actinium series either at $z=88$, $a=223$ or $z=86$, $a=219$—is unlikely since the expulsion of α-particles by actinium ($z=89$, $a=227$) has not been observed, but it appears possible. This second possibility would form a branch of the actinium series, and if such exists the branching ratio at actinium must be very small. The third possibility is that a branch occurs at actinium A ($z=84$, $a=215$). There is nothing to be said against this, as the possibility that a small proportion of β-particles accompanies the α-particles of actinium A has not been

* See Part I., *loc. cit.* p. 646.

tested experimentally, and would indeed be a very difficult thing to substantiate if it exists.

The lower series differs from the actinium series in that it keeps more particularly to elements of odd atomic number. There are again three alternative routes, but all pass through $z=87$, $a=221$ and $z=85$, $a=217$, and one of them passes through all of the elements of odd atomic number in its course. The relation of these to the hypothetical series of Part I. of this paper is illustrated in the figure. The hypothetical series is identical with one of the possibilities as far as the point marked X ; it then continues along the dotted line and joins the series again at $z=83$, $a=213$, and continues with it to $z=83$, $a=209$ (bismuth).

If the lower series exists its long-lived members are $z=91$, $a=233$, the apparent head of the series ; $z=87$, $a=221$; $z=85$, $a=217$, with $z=83$, $a=209$ as a possible end-product. It should consequently be looked for in minerals containing tantalum, but it need not exist in minerals containing thorium or uranium. Uranium might have an isotope 237 which by an α- and a β-change is transformed into the head of this series, but if so it is more complex than is to be expected ; the element $z=93$, $a=237$ is also a possible parent, but it, like its homologues, the missing elements 75 and 43, is probably unstable. These possibilities are indicated in the figure by dotted lines. However the series goes in its earlier stages, it ought not to pass through the element X in the way anticipated in Part I. of this paper. If it goes through X, X emits β-not α-particles and is transformed into a body about whose period nothing is known. This anticipation is consistent with our failure to find X experimentally, because, as is well known, the ionization contributed by a β-particle relative to that contributed by an α-particle is small. It may be argued, however, that this lower series is an unlikely one for the following reason. It is to be expected on general grounds that series whose members have odd atomic weights pass through the odd elements, and those whose members have even atomic weights through the even elements. The upper series in the figure may run either through even or odd elements, and it is known experimentally that it avoids the elements 85 and 87 and passes through elements 86, 84, and 82. The possibility of passing through even elements appears to be partly excluded from the lower series, and if it be not possible for a series to pass through the elements 87 and 85, the series (if it ever starts) may come to an end at the product which

would otherwise have been transformed into an isotope of element 87.

In the form the series are given in Table VI. and the figure, element 87 is simple with a mass-number of 221. Element 85 may also be regarded as simple with a mass-number of 217 until its possible second isotope 215, a branch product of actinium A, is discovered.

Summary.

(1) A search has been made in pitchblende, in thorianite, and in a preparation of radium for an isotope of radon, thoron, and acton expelling α-particles with an anticipated period of 70 minutes. This was unsuccessful.

(2) It is concluded either that, if this hypothetical emanation exists and expels α-particles, its period must be greater than 4 hours or less than 4 minutes; or that, if its period lies between the above limits, the number of atoms breaking up per second must be less than a value which varies between $\frac{1}{140}$ for the higher limit of period and $\frac{1}{2350}$ for the lower, of that of a member of the radium series in pitchblende or in thorianite.

(3) It is to be anticipated theoretically that there are only three out of four possible radioactive series which have members of atomic number 86 emitting α-particles. The fourth, if it exists, should arise from an isotope of protoactinium having an atomic weight of 233, pass through the missing elements 87 and 85, and end in bismuth.

(4) The principal isotopes of elements 91, 85, and 87 are calculated to be 233, 221, and 217 respectively. Elements 85 and 87 are probably simple.

We wish to thank the Government Grant Committee of the Royal Society for providing us with the instruments and materials employed in this work.

Dr. Lee's Laboratory,
Christ Church, Oxford,
March 1924.

XXXIII. *Scattering of Light by very big Colloidal Particles.*

By Was. Shoulejkin, *Professor of Physics, Higher Technical School, Moscow* *.

1. *Introduction.*

THE theory of light scattering developed by Lord Rayleigh †, and perfectly confirmed by a series of precise experiments, relates to the case of light falling on very small particles whose diameter is many times smaller than the wave-length of light.

In this case only do the relations stated by Lord Rayleigh allow us to define the brightness of light, radiated by a particle at some angle to its previous direction, as well as the polarization of the scattered light. Such particles as, for example, the molecules of gas, whose light-scattering has been thoroughly studied by Abbot and Fowl ‡ and J. Cabannes §.

But if one turns from molecules to colloidal particles—to colloidal solutions of resins, oil emulsions, etc.—the picture changes drastically: one notices already by sight that the scattering of light is here unsymmetrical towards the planes perpendicular to the incident rays. Light is brightest along directions not far away from the previous one, and is least bright in the opposite direction, whereas Rayleigh's formula gives a symmetrical distribution ‖.

If one studies the polarization of light scattered at different angles to the previous direction, it appears that the maximum of polarization corresponds to azimuth considerably greater than 90°, and here also polarization is incomplete.

All this shows that the laws of scattering of light by big particles vary greatly from those of the scattering by particles which are small in relation to the wave-length, and this difference is the greater, the coarser the particles.

The problem of scattering of light by particles of any dimension has been studied in general by G. Mie ¶, taking into account also the absorption of light by the particles

* Communicated to the Scientific Institution of Moscow, November 21, 1922.

† Lord Rayleigh, Phil. Mag. (4) xli. (1871); (5) xii. (1881); (5) xlvii. (1899).

‡ Abbot & Fowl, Astrophys. Journ. xxxiv. p. 203 (1911); xxxviii. p. 392 (1913).

§ J. Cabannes, *Annales de Physique*, xxv. p. 1 (1920).

‖ The experimental measurements have been made originally by Ramanathan, Phil. Mag. xlvi. p. 543 (1923).

¶ G. Mie, *Ann. d. Phys.* xxv. p. 377 (1908).

whose electrical conduction is not zero. But with a growth in the size of the particles the difficulties of calculation grow also rapidly, being at last rather serious.

Therefore Mie's studies were pursued only so far as to deal with particles a third of the size of the wave-length.

The present article fills up the gap between the small particles and *those of any size* (to the limit of infinitely big ones in comparison with the wave-length). In solving this problem we shall use the methods of the elaborate studies of Mie, but we shall limit our case to particles which have the ideal properties of a dielectric.

2. *The Theory of Mie.*

A flat wave falls on a spherical particle placed at the pole of a system of coordinates (r, ϑ, ϕ). By an integration of Maxwell's equations for the field inside and outside of the particle, and solving them together with the equations for a flat wave, Mie obtains expressions for the amplitudes of waves radiated by the particle in all directions and superposed on a flat wave.

As the common integral of Maxwell's equations includes a series of partial solutions, the whole radiation of the particle can be divided into an infinite number of partial waves. If ν be the number of partial waves and x be put equal to $\frac{2\pi \cdot r}{\lambda}$, where r is the distance of the pole and λ the wave-length of light *in the surrounding solvent*, the components of the amplitudes of the electrical vectors can be expressed in accordance with G. Mie as follows :—

$$\left.\begin{aligned}
E_r &= \sum_1^\infty \nu\, a_\nu \cdot i \cdot \frac{K_\nu(-x)}{x^2} \cdot P_\nu ; \\
E_\vartheta &= \sum_1^\infty \nu \left[\frac{a_\nu \cdot i}{\nu(\nu+1)} \cdot \frac{K_\nu'(-x)}{x} \frac{\partial P_\nu}{\partial \vartheta} \right. \\
&\qquad \left. + \frac{p_\nu}{\nu(\nu+1)} \cdot \frac{K_\nu(-x)}{x \cdot \sin\vartheta} \cdot \frac{\partial \mathfrak{P}_\nu}{\partial \phi} \right] ; \\
E_\phi &= \sum_1^\infty \nu \left[\frac{a_\nu \cdot i}{\nu(\nu+1)} \cdot \frac{K_\nu'(-x)}{x \cdot \sin\vartheta} \frac{\partial P\nu}{\partial \phi} \right. \\
&\qquad \left. + \frac{p}{\nu(\nu+1)} \cdot \frac{K_\nu(-x)}{x} \cdot \frac{\partial \mathfrak{P}_\nu}{\partial \vartheta} \right] .
\end{aligned}\right\} \quad (1)$$

Here $K_\nu(-x)$ (and $K_\nu'(-x)$) is a function (and its derivative) entering into the integral of Maxwell's equations

which depends upon r; P_ν and $\mathfrak{P}_\nu$ are functions of ϑ and ϕ. The magnetic components M_r, M_ϑ, and M_ϕ are expressed similarly.

The functions a_ν and p_ν entering into all expressions are defined by border conditions; these are complex functions, depending upon the wave-length, the radius of the particle, and the index of refraction of the material of the particle in relation to the outer medium m'.

The relations are considerably simplified if one supposes that the point where the field of light is studied is as far from the particle as r, a distance very great in comparison with its radius ρ.

In accomplishing corresponding modifications, G. Mie passes from amplitudes of vectors to the values of intensity of light radiated by the particle in all directions. The intensity of the incident light is taken as a unit. For the definition of the polarization of the scattered light Mie investigates two of its components: (1) the radiation I_I whose electrical oscillations are perpendicular to the plane of sight, and (2) the radiation I_{II} whose electrical oscillations are in the plane of sight itself (but, indeed, also perpendicular to the ray of sight).

If the scattered ray investigated makes an angle $(\pi-\gamma)$ with the ray falling on the particle, then the intensities I_I and I_{II} will be expressed according to Mie as:

$$\left.\begin{aligned} I_I &= \frac{\lambda^2}{4\pi^2 r^2}\left|\sum_1^\infty \nu\left\{\frac{a_\nu}{\nu(\nu+1)}\Pi_\nu - \right.\right. \\ &\qquad \left.\left. + \frac{p_\nu}{\nu(\nu+1)}(\Pi_\nu^{\cdot}\cdot\cos\gamma - \Pi_\nu'\sin^2\gamma)\right\}\right|^2; \\ I_{II} &= \frac{\lambda^2}{4\pi^2\cdot r^2}\left|\Sigma\nu\left\{\frac{a_\nu}{\nu(\nu+1)}(\Pi_\nu\cdot\cos\gamma - \Pi_\nu'\cdot\sin^2\gamma)\right.\right. \\ &\qquad \left.\left. + \frac{p_\nu}{\nu(\nu+1)}\cdot\Pi_\nu\right\}\right|^2. \end{aligned}\right\} \quad (2)$$

The sign $|\ |^2$ shows that the quadrate of the absolute value of the complex in the parenthesis is taken. Π_ν are spherical functions, Π_ν' their first derivatives on $\cos\gamma$.

The summation I_I+I_{II} gives the full intensity of the rays scattered under the angle γ, and the difference I_I-I_{II} is the surplus of polarized light. If the difference is positive, the light is polarized so that the electrical oscillations are perpendicular to the plane of sight; if it is negative, the electrical oscillations are in the plane of sight. The number ν of the partial waves which can be considered sufficient for

calculations depends upon the size of the particle in relation to the wave-length.

We shall calculate four cases:

$$(a)\ \mathrm{Lim}\frac{\rho}{\lambda}=0;\quad (b)\ \frac{2\pi\rho}{\lambda}=1;\quad (c)\ \frac{2\pi\rho}{\lambda}=3;$$

and finally $(d)\ \mathrm{Lim}\frac{\rho}{\lambda}=\infty$.

Let us take as a colloid a substance with an index in relation to the medium $m'=1{\cdot}32$. This corresponds to an emulsion of paraffin oil in water or to drops of condensed vapour in air. The results obtained can also, with some modifications, be applied to the case $m'=\frac{1}{1{\cdot}32}$, corresponding to bubbles of gas suspended in water.

3. *The very small Rayleigh's Particles.*

In this case the radiation consists in the first partial wave: $\nu=1$. Besides $p_1=0$ in equations (2), of the two complex functions a_1 and p_1 only a_1 appears where

$$a_1=2\alpha^3\frac{m'^2-1}{m'^2+2},$$

where α is an abbreviation for $\frac{2\pi\rho}{\lambda}$.

Again, $\Pi_1=1$ and $\Pi_1'=0$. On putting these values into (2), we have:

$$\mathrm{I_I}=\frac{\lambda^2}{4\pi^2r^2}\left|\frac{a_1}{2}\right|^2;\quad \mathrm{I_{II}}=\frac{\lambda^2}{4\pi^2r^2}\left|\frac{a_1}{2}\cos\gamma\right|^2.$$

And finally:

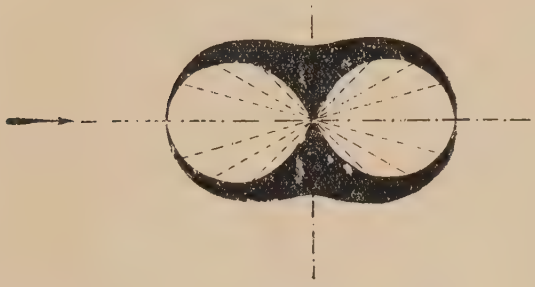
$$\mathrm{I_I}+\mathrm{I_{II}}=\frac{16\pi^4\cdot\rho^6}{\lambda^4r^2}\left[\frac{m'^2-1}{m'^2+2}\right]^2(1+\cos^2\gamma);$$

$$\mathrm{I_I}-\mathrm{I_{II}}=\frac{16\pi^4\cdot\rho^6}{\lambda^4r^2}\left[\frac{m'^2-1}{m'^2+2}\right]^2(1-\cos^2\gamma).$$

This is evidently Rayleigh's law of scattering. On plotting out graphically the intensity of scattered light along polar coordinates in some scale on radii-vectores, we get the curves of fig. 1. The outer curve represents the full brightness of the dispersed light, and the parts of the vectors between the

outer and the inner one (in the shaded part) the admixture of polarized light. The maximum of polarization corresponds

Fig. 1.



to an angle of 90° to the incident rays; the polarization is here complete, and the electrical oscillations are perpendicular to the plane of sight.

4. *Particles of a Diameter about a third of the Wave-length of Light.*

Let us suppose $\frac{2\pi\rho}{\lambda}=1$.

In this case, as Mie has done, one has to take into consideration the first ($\nu=1$) and the second ($\nu=2$) partial wave. But out of all the complex values a_1, p_1, a_2, and p_2, the last one (p_2) can be still left out of account. The remaining coefficients are equal to the following values, if one drops the common multiplicator e^{-i} which does not influence the result:

$$\begin{aligned} a_1 &= \ \ 0{\cdot}156 - i\,.\,0{\cdot}324 \\ p_1 &= -0{\cdot}025 + i\,.\,0{\cdot}040 \\ a_2 &= -0{\cdot}017 + i\,.\,0{\cdot}027 \end{aligned} \qquad \text{with} \qquad \begin{aligned} \Pi_1 &= 1. \\ \Pi_1' &= 0. \\ \Pi_2 &= 3\cos\gamma. \\ \Pi_2' &= 3. \end{aligned}$$

In simplifying the calculations we drop in the formula (2) the multiplier $\frac{\lambda^2}{4\pi^2 r^2}$ before the parenthesis, because at present we want to find the law of the distribution of energy around the particle, and not the absolute brightness of light.

Therefore, out of the modified equations (2) we determine the values j_{I} and j_{II}, proportional to I_{I} and to I_{II}.

Equations ready for calculations have the following aspect:

$$j_{\mathrm{I}} = \left| \frac{a_1}{2} + \frac{a_2 + p_1}{2} \cos\gamma \right|^2 ;$$

$$j_{\mathrm{II}} = \left| \frac{a_1}{2} \cos\gamma + \frac{a_2}{2} \cos 2\gamma + p_1 \right|^2 .$$

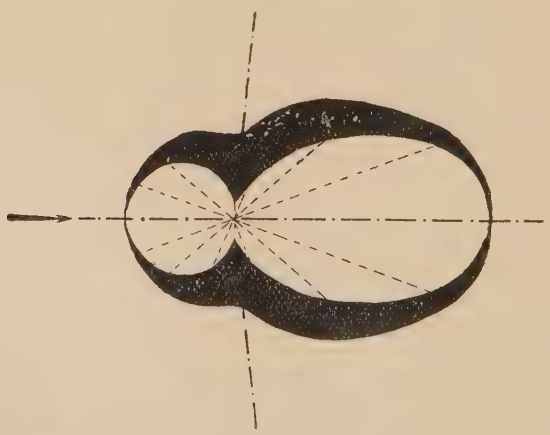
The results of the calculations are given in Table I.

TABLE I.

Angle γ ...	0°.	20°.	40°.	60°.	90°.	120°.	140°.	160°.	180°.
The full brightness (relat.).	0·0390	0·0387	0·0380	0·0360	0·0325	0·0462	0·0667	0·0875	0·0925
The polarized light.	0	0·0020	0·0070	0·0155	0·0297	0·0327	0·0212	0·0060	0
Percentage of polarized light.	0	5·2	18·5	43	91	71	32	6·8	0

The law of radiation is graphically represented in fig. 2. Here, as in fig. 1, the radii-vectores of the outer curve

Fig. 2.



express the full brightness of light, and their parts in the shaded surface the admixture of polarized light, where the plane of polarization is the same (that of Rayleigh) as in fig. 1. The maximum of polarization is here removed from

90° towards the direction of the falling rays. The polarization is *everywhere complete*. The whole curve is more symmetrical; its left part is contracted, its right part is more developed than that of Rayleigh's in fig. 1.

5. *Particles whose Diameter is approximately equal to the Wave-length.*

Let us suppose $\frac{2\pi\rho}{\lambda}=3$.

With this size of a particle one has to consider several partial waves, which rather complicates calculations. After a determination of the amplitudes of several partial waves, we found that it is possible to ignore waves from the 4th degree upwards ($\nu=4$). Therefore one has to summarize three separate electrical and three separate magnetic oscillations for $\nu=1$, $\nu=2$, and $\nu=3$. The coefficients a_1, p_1; a_2, p_2; a_3, p_3 in the formula (2) determined by border conditions were found to be:

$$a_1=-1{\cdot}7\ +i\,.\,1{\cdot}25\,; \qquad p_1=-0{\cdot}224-i\,.\,3{\cdot}32.$$
$$a_2=\ 2{\cdot}54-i\,.\,1{\cdot}27\,; \qquad p_2=-2{\cdot}64\ +i\,.\,1{\cdot}48.$$
$$a_3=\ 1{\cdot}51-i\,.\,0{\cdot}12\,; \qquad p_3=\ 0{\cdot}676+i\,.\,0{\cdot}029.$$

Further:

$$\Pi_1=1\,; \quad \Pi_2=3\cos\gamma\,; \quad \Pi_3=7{\cdot}5\cos^2\gamma-1{\cdot}5.$$
$$\Pi_1=0\,; \quad \Pi_2=3\,; \quad \Pi_3=15\cos\gamma.$$

Instead of I_I and I_{II} let us calculate, as in the former section, the values j_I, and j_{II}, proportional to them. After some simplifications we obtain the following expressions for j_I and j_{II}:

$$j_I=|\,Q_I\cos^3\gamma+R_I\cos^2\gamma+S_I\cos\gamma+T_I\cos 2\gamma+U_I\,|^2\,;$$
$$j_{II}=|\,Q_{II}\cos^3\gamma+R_{II}\cos^2\gamma+S_{II}\cos\gamma+T_{II}\cos 2\gamma+U_{II}\,|^2.$$

Here:

$$Q_I=\frac{22{\cdot}5}{12}p_3\,; \qquad Q_{II}=\frac{22{\cdot}5}{12}a_3\,.$$

$$R_I=\frac{7{\cdot}5}{12}a_3\,; \qquad R_{II}=\frac{7{\cdot}5}{12}p_3.$$

$$S_I=\frac{p_1+a_2}{2}-\frac{16{\cdot}5}{12}p_3\,; \qquad S_{II}=\frac{a_1+p_2}{2}-\frac{16{\cdot}5}{12}a_3.$$

$$T_I=\frac{p_2}{2}\,; \qquad T_{II}=\frac{a_2}{2}\,.$$

$$U_I=\frac{a_1}{2}-\frac{a_3}{8}\,; \qquad U_{II}=\frac{p_1}{2}-\frac{p_3}{8}\,.$$

The numerical values for those ten complex coefficients are given in Table II.

Table II.

	I.	II.
Q.....	$1{\cdot}27 + i\,.\,0{\cdot}054$	$-2{\cdot}83 - i\,.\,0{\cdot}225$
R.....	$-0{\cdot}945 - i\,.\,0{\cdot}750$	$0{\cdot}424 + i\,.\,0{\cdot}018$
S.....	$0{\cdot}230 - i\,.\,2{\cdot}33$	$-0{\cdot}085 + i\,.\,1{\cdot}525$
T.....	$-1{\cdot}32 + i\,.\,0{\cdot}740$	$1{\cdot}27 - i\,.\,0{\cdot}630$
U	$-0{\cdot}660 + i\,.\,0{\cdot}640$	$-0{\cdot}197 - i\,.\,1{\cdot}664$

The calculation of j_{I} and j_{II} for nine different azimuths gives the full (relative) brightness of dispersed light $j_{\mathrm{I}} + j_{\mathrm{II}}$ as well as the admixture of polarized light $j_{\mathrm{I}} - j_{\mathrm{II}}$ (see Table III.).

Table III.

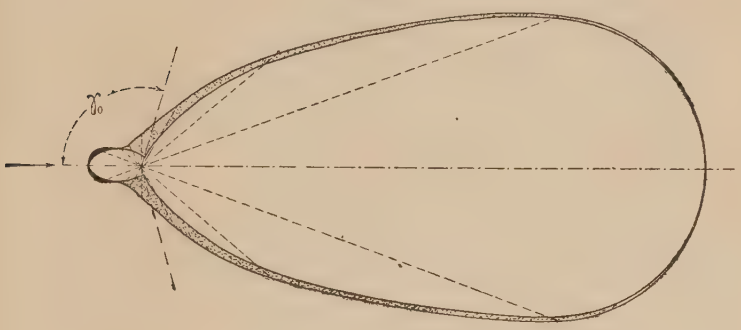
Angle γ ...	0°.	20°.	40°.	60°.	90°.	120°.	140°.	160°.	180°.
Full brightness (relative).	6·0	5·03	3·06	2·70	3·56	7·94	19·7	50·5	64·4
Admixture of polarized light.	0	+0·25	−0·13	−1·06	−2·68	−3·6	−1·45	−0·5	0
Percentage of polarized light.	0	+5	−4·2	−38·1	−75	−45	−7·4	−1	0

The sign (−) before almost every number of the third line shows that the plane of polarization is turned at an angle of 90° in relation to that of Rayleigh, and the electrical oscillations are in the plane of sight.

Fig. 3 shows the law of radiation represented, as before, in a polar system of coordinates. It is evident that there is little in common between scattering of light by small (§ 3) and big particles, and that the curve of radiation is sharply deformed, developing in the direction of incident rays.

Even the polarization is here, as we have seen, quite in a different plane. Rayleigh's polarization (§ 3) has been preserved only for very small azimuths (where the surface between the outer and inner curve is *shaded*; but where this surface is dotted the plane of polarization is perpendicular to that of Rayleigh). The maximum of polarization is still more displaced from 90° than in case § 4, and the degree of polarization even at this optimal angle is still less complete.

Fig. 3.



What is the physical meaning of this change in the character of scattering? What does such a deformation of the curve of radiation, such a displacement of the maximum of polarization and even of the plane of polarization, signify? We shall endeavour to solve these questions in § 6, investigating the last of the possible cases with very big particles, for which the relation $\frac{\rho}{\lambda}$ tends towards infinity.

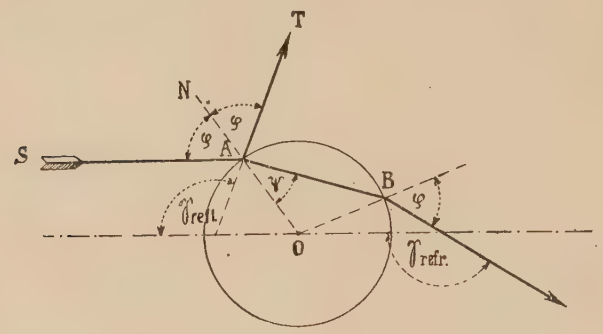
6. *The biggest possible Particles.*

In the case of such big particles, for which $\text{Lim}\ \frac{\rho}{\lambda} = \infty$, we shall not proceed with the calculations used above, but we shall use quite different methods.

It is easy to conjecture that such big spherical dielectric globes will simply refract and reflect rays falling upon them, and that the brightness of the reflected and refracted rays radiated by these balls in all directions can be calculated on a basis of common propositions.

Fig 4 shows the details of this case. Let one of the parallel rays (SA), shining upon the globe, fall upon it in the point A, forming with the normal AN an angle $SAN=\phi$. A part of the light-energy will be reflected at an angle SAT to the ray SA, so that evidently $SAT=2\phi$.

Fig. 4.



Therefore for reflected rays $\gamma=2\phi$. The brightness of the ray reflected at such an azimuth can be found from the relation

$$\left.\begin{aligned} &I_{refl.}=I_{inc.}\,.\,\Phi\,.\cos\phi,\\ &\text{where there is an abbreviation,}\\ &\Phi=\frac{1}{2}\frac{\sin^2(\phi-\psi)}{\sin^2(\phi+\psi)}\left[1+\frac{\cos^2(\phi+\psi)}{\cos^2(\phi-\psi)}\right]^2. \end{aligned}\right\} \quad (3)$$

The admixture of polarized light is

$$\left.\begin{aligned} &(I_{refl.})_{polar.}=I_{inc.}\,.\,\Phi'\,.\cos\phi,\\ &\text{where}\\ &\Phi'=\frac{1}{2}\frac{\sin^2(\phi-\psi)}{\sin^2(\phi+\psi)}\left[1-\frac{\cos^2(\phi+\psi)}{\cos^2(\phi-\psi)}\right]^2. \end{aligned}\right\} \quad (3')$$

The plane of polarization will be, evidently, perpendicular to that of Rayleigh, because electrical oscillations will be in the plane of sight.

At an angle $\phi_0=\text{arctang}\,(m')$ the reflected ray will be completely polarized. Therefore a ray with an azimuth $\gamma_0=2\phi_0=2$ arctang (m') will be completly polarized. In our case, where $m'=1{\cdot}32$ the value of γ_0 will be $\gamma_0=105^\circ\,40'$.

The calculations of brightness of the reflected light are given in Table IV., where the brightness of the incident light is taken as a unit.

TABLE IV.

Angle γ	10°.	20°.	30°.	40°.	60°.	90°.
The full brightness of the reflected light.	0·017	0·017	0·018	0·0182	0·0169	0·0182
Admixture of polarized light (in a reflected ray).	0·000	0·0010	0·0020	0·0036	0·0077	0·0180

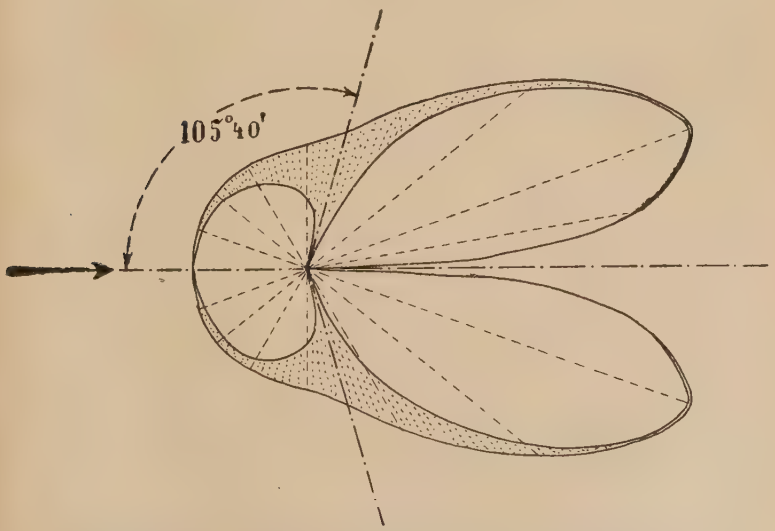
120°.	140°.	150°.	160°.	170°.	179° 40′.
0·0287	0·0441	0·0539	0·0600	0·0506	0·0030
0·0285	0·0425	0·0510	0·0190	0·0076	0·000

Therefore it is evident that if $\gamma=0$,

$$I_{refl.}=\left(\frac{m'-1}{m'+1}\right)^2=0{\cdot}017\,.\,I_{inc.},$$

and that if $\gamma=180°$, $I_{refl.}=0$ (because $\cos\phi=0$).

Fig. 5.



The same law of reflexion at different azimuths is represented graphically in fig. 5.

But the full energy of "scattering" by a spherical globe is evidently composed of two parts: one of them, the energy of the wave reflected from the surface, we have already taken into account. It remains to calculate the energy of rays which have penetrated through an absolutely transparent dielectric globe and are refracted at its surface.

We see in fig 4 that a refracted ray will come out of the ball under the same angle ϕ to the normal line in the point of exit (B) at which it previously fell upon the surface of the ball in the point A. Therefore the brightness of the reappearing ray will be found from the relation

$$I_{refr.} = I_{inc.} \cdot (1-\Phi)^2 \cdot \cos\phi,$$

where Φ has its previous significance. The azimuth of this ray is easily found from the geometrical relations; it will be

$$\gamma_{refr.} = 180^\circ - 2(\phi - \psi).$$

The values for $I_{refl.}$ calculated for a series of angles $\gamma_{refr.}$ (corresponding to values of the angle $\phi = 5^\circ, 10^\circ, 15^\circ$, etc.) are represented in Table V.

Table V.

Angle $\gamma_{refr.}$ ...	177° 40′.	175° 20′.	172° 40′.	170° 0′.	164° 40′.	155° 0′.
Brightness of light which passes through the ball.	0·967	0·950	0·933	0·907	0·836	0·709

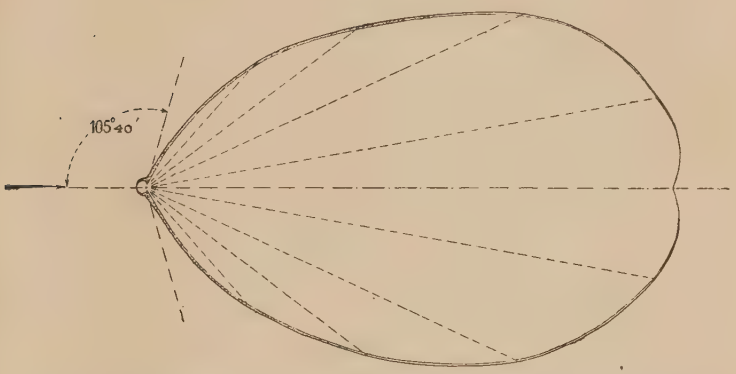
142° 0′.	131° 0′.	124° 20′.	116° 20′.	108° 0′.	98° 40′.
0·450	0·260	0·162	0·075	0·015	0·000

The polarization of these rays can be determined from Table IV. For a precise calculation of the "scattering" of energy, one has to take into account the secondary, tertiary, etc. refractions of rays inside the globe, but this feebly influences the final result, and we omit them. In summarizing the energies of rays (a) reflected by the surface of

the ball and (*b*) those which pass through it, we find the final law of scattering graphically represented in fig. 6.

We can see that this fig. 6 resembles fig. 3, which has been obtained on the proposition of the theory of scattering of light for particles whose diameter is approximately equal to the wave-length $\left(\frac{2\pi\rho}{\lambda}=3\right)$. And this likeness is not occasional or external, but very *deep* and of an inner origin.

Fig. 6.



If one considers the polarization of rays in both cases, in order to prove the correctness of the above said, the plane of polarization just at the position of the maximum of polarization is the same in both cases (in the latter case the polarization will be also incomplete, even at an optimal angle of 105° 40′, because upon a completely-polarized wave of fig. 5 another not fully-polarized wave, which has passed through the globe, is superposed).

The law of scattering itself, found in § 5, has now a clear physical meaning: the greater development of the right part of the curve with a growth of the diameter of the particles is caused by *an emerging refracted wave* which has passed through a dielectric ball. The maximum of polarization, corresponding in Rayleigh's particles to an angle of 90°, *is striving for an optimal angle* γ_0, *which is equal to a double angle* ϕ_0 of a complete polarization of the reflexion (the tangent of the latter is equal to the index of refraction m').

Conclusion.

1. The distribution of scattered energy of light around a radiating particle of a turbid medium (dielectric in an ideal state) is subject to Lord Rayleigh's formula, if diameters of

the particles 2ρ are included in the limit $0 < 2\rho < \frac{1}{3}\lambda$. At an angle $\gamma_0 = 90°$ the scattered light is completely polarized (the electrical oscillations are perpendicular to the plane of vision).

2. Already at $2\rho \cong \frac{\lambda}{3}$ one notices a definite asymmetry of dispersion, so that along the direction of incident rays the brightness of the scattered light is 2·5 times greater than in the opposite direction (these calculations have been made for a relative index of refraction $m' = 1{\cdot}32$). The angle of maximal polarization is displaced from 90° in the direction of incident rays. The polarization is everywhere incomplete, but in the same plane as in point 1.

3. With diameters bigger than $2\rho \cong \lambda$, the asymmetry is still greater; with $2\rho \cong \lambda$ and with $m' = 1{\cdot}32$ the brightness of light dispersed in the direction of incident rays is approximately 11 times greater than the brightness in the opposite direction. The maximum of polarization is displaced still more from the angle 90°, tending in the limit to the angle $\gamma_0 = 2 \arctan(m')$. The plane of polarization itself completely changes with such dimensions of the particles; it gets perpendicular to the plane of polarization of Rayleigh's particles, *i. e.* electrical oscillations are in the plane of sight.

4. This plane of polarization as well as the character of distribution of the dispersed energy, *from these dimensions of particles upwards, does not change any more* until just the greatest dimensions of particles which can be studied by common methods *applying the laws of refraction* and *reflexion of light*. The greater and still greater development of the curve in the direction of incident rays is due to the wave which *has passed through* the dielectric globe.

5. In limits with dimensions of particles infinitely greater than the length of the wave, the brightness of light scattered in the direction of incident rays is 52 times greater than the brightness in the opposite direction (if $m' = 1{\cdot}32$). The angle of maximal polarization is in this case equal to 105° 40′.

6. There is, therefore, a smooth continuous change from scattering of light to its reflexion and refraction.

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XXXIV. *Notes on the Constitution of Spectra.* *By* W. M. Hicks, *Emeritus Professor of Physics, University of Sheffield.*

I. In re *the Oun.*

THE opinion has been expressed that the discovery of isotopes has invalidated the evidence for the existence of the oun and the part it plays in the constitution of sequence terms. This is, however, based on a misconception of the evidence. When it is remembered that the first discovery of the oun effect was led up to by the general belief at the time that the doublet and triplet separations depended in some way on the squares of the atomic weight, such a misconception is perhaps natural. If the problem had been considered after the publication of Aston's researches on isotopes, it would probably have been tested on the basis of squares of atomic numbers. In that case the result would have been nugatory † and the discovery of the oun effect would have been left for some future investigator.

The magnitude of all doublet, triplet, and satellite separations is a secondary effect depending on definite changes in the denominator of the function N/D^2 which gives the value of the terms of a sequence. Thus in a doublet series, the limits are given by N/D^2 and $N/(D-\Delta)^2$, so that the separation of the two series is $\nu = N/(D-\Delta)^2 - N/D^2$. If we wish to determine how the separation (ν) depends on any natural quantity, it is the Δ and not the ν which we have to study. A consideration of these Δ showed, that if w denote (atom. wt.)/100 then in *all* cases where the series were known the Δ (or Δ_1, Δ_2 in triplets) were integral multiples of a quantity $= (90{\cdot}445 \pm {\cdot}005)w^2$, within observational errors spectroscopic or chemical. In fact, with the more accurate data of to-day any alteration of a multiple by unity entirely upsets the relation. That it is possible to do this with elements whose atomic weights range from 23 (Na) to over 200 (Hg, Tl, Ra) is in itself a remarkable result. But it is then found that the satellite separations in *d* and *f* sequences, as well as the enhanced doublets in group II. (ionized atoms) also depend in a similar way on multiples of the same oun, and indeed that other effects, not further dealt with in this note, depend on oun values.

This dependence of all the various separations on the oun opens up a possibility of an independent and purely spectral determination of the oun values, especially in cases where

* Communicated by the Author.

† See 'Analysis of Spectra,' p. 149.

triplet series occur or where the successive spectra of multiply ionized atoms are known*. To do this with confidence accurate spectroscopic measures are required, especially for D and F satellites where observation errors are multiplied by large factors in the corresponding Δ. Ultimately we may hope to obtain a large number of oun values thus independently obtained, and then it will be possible to consider directly their dependence on the atomic weight.

Meanwhile, on the evidence as it stands at present we can hardly escape from the conclusion that as an experimental fact the oun is proportional to the square of the atomic weight, that is to a quantity which, in at least a large number of cases, corresponds to no physical entity. Possibly a way out of the difficulty may be indicated by the following considerations. To fix ideas take the case of an element with two isotopes A, B. It is usual to *explain* the observed atomic weight as the statistical mean of the two isotopes occurring in their respective numbers. The ratio in their numbers appears as a quite definite one, the same from whatever source the element tested has been taken. Why, in the building up—or degrading—of successive elements, do we find that for each particular one the isotopes are always in this ratio? If the numbers were equal we might take it as due to pure chance, but this explanation is not here tenable. There must be some cause which, in the building up of an element, settles in a precise way the probability of the entrance of each isotope, and this cause must depend in some way on the constitution of the element itself. Does this cause also affect the different energy levels which in any sequence produce the doublet and triplet separations? If so, the oun depends on this quality directly, and only in a secondary sense on the observed atomic weight, because this latter also depends on it.

II. *The Aluminium Oun.*

The recent remarkable work of Paschen † on the spectra of the singly and doubly ionized atom of aluminium enables

* *E. g.* in Cd with very accurate measures:—

Cd.		Cd^+.	
Δ_1.	$23105{\cdot}83 = 203 \times 113{\cdot}819$.	Δ.	$27348 = 240 \times 113{\cdot}94$.
Δ_2.	$10370{\cdot}33 = 91 \times 113{\cdot}959$.	σ.	$4314 = 38 \times 113{\cdot}53$.
$\Delta_1+\Delta_2$.	$33476{\cdot}16 = 294 \times 113{\cdot}864$.		
$\sigma_1+\sigma_2$.	$3303 = 29 \times 113{\cdot}89$.		

The satellite in Cd^+(4314) depends on two ultra-violet lines with considerable possible errors in wave number. It agrees with 113·864 within possible errors.

† *Ann. der Phys.* lxxi. pp. 142, 537 (1923).

us to illustrate the exactness of the oun relation in this element very fully. It must be noted that values of the Δ obtained with enhanced spectra are specially accurate, since on account of the 4N, 9N, etc., relation, their percentage uncertainties are very much diminished. In the present case in addition the observations themselves are of the first order of accuracy. For the neutral atom the oun relations for the doublet separations and the satellite separations for D(2) and D(3) are very fully obeyed *, but as the oun values for all the early elements in any periodic group are small, their evidential value for proving the reality of the reality of the relation was not great. The new spectra, however, afford increased data with striking agreement.

The various data from the three spectra are here given. Paschen's values for the terms in Al II, Al III are all affected with the same unknown error, but it is small and the effect on our deduced values is inappreciable. We shall use the value of δ (4 ouns) as given in the 'Analysis' and determined from the doublet separation of Al I. In the case of triplets the values for the sum of the separations are also given, because in the majority of elements there is a small "triplet modification" as between ν_1 and ν_2, although $\nu_1+\nu_2$ is normal. This modification, however, is almost negligible in the early elements of a group.

$$\delta = 4\delta_1 = 26{\cdot}5465 \pm {\cdot}0045.$$

		Sep.	Δ.	
Al I Doublet.	$p(1)$.....	112·038±·010	1752·07±·30	66δ
	$d(2)$.....	1·33	110	$4\frac{1}{4}\delta = 112{\cdot}8$
	$d(3)$.....	4·49	823	$31\delta = 822{\cdot}9$
Al II Triplets.	$p(1)$.....	125·5	1075	$40\frac{1}{2}\delta = 1075{\cdot}1$
		61·8	529	$20\delta = 530{\cdot}9$
		187·3	1604	$60\frac{1}{2}\delta = 1606{\cdot}0$
	$d(2)$.....	2·16	53·5	$2\delta = 53{\cdot}1$
		1·12	27·8	$\delta = 26{\cdot}5$
		3·28	81·3	$3\delta = 79{\cdot}6$
	$f(3)$.....	2·81	194·0	$7\frac{1}{4}\delta = 192{\cdot}5$
		2·09	143·7	$5\frac{1}{2}\delta = 146{\cdot}0$
		4·90	337·7	$12\frac{3}{4}\delta = 338{\cdot}5$
	F(3) ...	47·53	3286·2	$123\frac{3}{4}\delta = 3285{\cdot}1$
Al. III Doublet.	$p(2)$.....	238·00	1606·2	$60\frac{1}{2}\delta = 1606{\cdot}0$
	$p(3)$.....	80·30	1592·0	$60\delta = 1592{\cdot}7$

It will be noticed that the Δ for $\nu_1+\nu_2$ in Al II and ν in

* 'Analysis' pp. 128, 136, misprints on p. 136 here corrected.

Al III have the same value $60\frac{1}{2}\delta$, although the $\nu_1+\nu$ and ν—187·3 and 238—are quite different. This illustrates the fact that the essential quantity to study is the Δ and not the separation observed.

III. *The Spectrum of Manganese.*

The S''' (2, 3) and D''' (2, 3, 4) sets were allocated by Kayser and Runge in 1894. Extensions up to $m=7$ were given in my 'Analysis of Spectra.' Catalan* has since given a very full discussion of the different series of this element. His work has brought to light a number of new facts and has been the occasion of extraordinarily interesting extensions by Sommerfeld of his descriptive theory of internal quantum numbers and by Landé of his empirical method of predetermining the Zeeman patterns, verified experimentally by Back. This note, however, has no reference to these questions, but considers only a few minor points relating to series arrangements. It is followed by a short excursus on the theory of displacement, illustrated by the higher orders of these series.

For $P'''_{123}(2)$ Catalan gives $\lambda=15263$, $n=6550$ and supports it by two suggested combinations $nn=27280{\cdot}20$, $27444{\cdot}65$ as $p_1 1-p_k 2$, $p_2 1-p_k 2$. As $p_2 1-p_1 1=173{\cdot}6$ the separation of these, 164·45, is too large for different k and too small for same k. The following are suggested as preferable (measures by Fritsch):—

	I.	λ.	*n*.	
$p_1 1-p_3 2'$	1,	3667·758	27257·79	
$p_1 1-p_2 2$	3,	3664·779	27279·95	
$p_1 1-p_1 2$	4,	3660·549	27311·47	173·80
$p_2 1-p_2 2$	3,	3641·579	27453·75	

These give for P(2) the set, in wave-number:—

6585·50
31·52
6553·98
22·16
6531·82

The separations are in the same ratio as in P(1) and of the order of magnitude to be expected. They also support Catalan's allocation of $\lambda=15263$ as a mean value of $P_{123}(2)$. His proposed set for P(3) give separations also in about the same ratio and of suitable magnitude. But with these two sets for P(2, 3) his $\lambda=6315$ for P(4) is doubtful, as indeed

* Trans. Roy. Soc. 223 A. p. 127.

he indicates. Its denominator would be 4·8376 as compared with 1·6305, 2·8047, 3·8360 for the others, and too small to be in step. We should expect one about 4·8516 corresponding to about $\lambda=6300$.

In the S''' we agree up to $m=5$, whilst Catalan gives a slightly different set for $m=6$ and none for $m=7$. The equation calculated from $m=2, 3, 4$ exactly reproduces the wave number for $m=5$. The formula may therefore be considered as very reliable. For $m=6$ it deviates very largely from Catalan's allocation, less from mine, but still outside observation errors. For $m=6, 7$ the calculated values fall in a region containing a large number of displaced lines, and are considered below in note IV. In D''' again Catalan gives up to $m=5$ only. We differ slightly for $m=5$, but again we come into a region of displacement also considered in note IV. The equations, with $N=109678{\cdot}7$, are

$$S_1''',\quad 41254{\cdot}06-N/\{m+1{\cdot}378714-{\cdot}067251/m\}^2$$

$$D_1''',\quad 41254{\cdot}06-N/\{m+\ {\cdot}904297-{\cdot}049476/m\}^2,$$

S being determined from the first three lines and D from the S(∞) and the first two lines. The ν separations show an anomalous ratio of 1·34, or say 4 : 3, instead of being greater than 2. They seem analogous to those of O, S, in group VI. with ratios 1·8, 1·6, although Se in the same group gives 2·5. The D sequence is also unusual in that the coefficient of $1/m$ is negative, but the outstanding interest of the D series is that the sequence *genus d* comprises five *species* in place of the three hitherto known. These species are analogous to those of the triplets hitherto recognized, in being formed by successive negative displacements. In the newly found single groups of multiplets on the contrary, they are formed by successive positive displacements.

The presence of triplets in an element of group VII., where according to Rydberg's rule we should expect doublets, is an anomaly for which Catalan's explanation is probably correct *. But another anomaly also occurs in connexion with the series which in other elements constitute a singlet system associated with the triplet. For the singlet systems to be expected we apparently get triplets. But if this is really the case, we have a new fact in spectral constitution, the evidence for which calls for careful examination. As a contribution towards this, the series arrangements are

* But see Sommerfeld, *Ann. d. Phys.* lxxiii. p. 217 (1924).

here discussed rather more fully than would otherwise be necessary.

For the singlet representatives he finds triplet systems in about the correct position and composed of lines of correct spectral behaviour. In addition there is another triplet system, parallel to this, in which the first members of each order are separated by 10967·75 from the corresponding line of the other. As this second series has separations 14·22, 8·70, in the ratio 5 : 3, we shall take it that its limit term belongs to a d sequence, that of the first being of the p type.

There can be little doubt but that the allocation of $s'1-p_2'''1$ is correct and from this, $s'1$ can be calculated (=59959·40). Regarding the first series as a split representative of a true S′, the first line gives with the above $s'1$ the limit $p_1 2$ as 24189·39. But if it is not, the series must be treated independently, and the formula calculated from the first three lines. The result is to give a limit 216 larger. The formula calculated with the supposed $p'2$ limit and the first two orders gives for the third ($m=3$) a line in error by 53A. This might seem decisive against the hypothesis, were it not that in these typical singlets, the first line is in general greatly out of step with the others, and a formula calculated with it unsuitable. It is found better to determine the formula from the next three lines, or as here, where the limit is given, from that and the second and third orders. The two formulæ are then, on the two hypotheses,

$$S_1^n, \quad n=24405{\cdot}17-N/\{m+{\cdot}484377-{\cdot}134311/m\}^2$$
$$S_1', \quad n=24189{\cdot}39-N/\{m+{\cdot}578576-{\cdot}294684/m\}^2,$$

where S^n refers to that of an independent narrow triplet, and S′ to that of a "singlet" system.

The first equation gives lines for $m=4$, 5 at $n=18868{\cdot}53$ and 20722·76. The former is close to two observed lines $(3n)$ 18866·95 and $(2n)$ 18870·10. Moreover, a line at (2) 29838·44 is separated from 18870 by the shift 10968·34, only ·6 greater than that between the two parallel series. Further, as this is the shift between the first lines of each order, it is supporting evidence that 18870 is $S_1(4)$ or close to it. But it does not show triplets with lines ν_1, ν_2 ahead. Indeed, the other line 18866·95 is the centre of a congeries of triplets. There is clear evidence of considerable displacement and linkage effects in both regions round 18870 and 29838.

The second formula gives for $m=1$ a line at λ2361A, quite impossible for the observed 2794A. For singlets,

especially with a large α, as here, we often find considerable discrepancies between observation and calculation for the first line, but in this case it is very excessive. On the other hand, the calculated lines for $m=4, 5$ are found with approximate triplets. The calculated have $n=18784{\cdot}95, 20589{\cdot}40$. As the matter is important from its bearing on general theory, the data are more closely discussed in the next note.

The annexed table gives the oun relations for different series. The values of the satellite separations of the normal D‴ series vary so greatly as given by different observers, that displacement in both terms or some unknown effect is clearly present and it is impossible to assign definite values. The separations for the first three orders of P are given, in which it should be remembered that those for P(2) are measured on the $p1-p2$ combinations and are consequently very accurate. The values for the "singlet" series and the dependent multiplets will depend on the limit adopted—S^n or S′. That of S^n may be in excess by an error <10. The S′ limit is definite within about ±1. Both are given, those depending on S′ in italics. Further, the values for the sum of the separations are also given, as owing to the "triplet modification" effect it is this to which the multiple law is applicable.

$$\delta=109{\cdot}233+{\cdot}36dv. \qquad dv<{\cdot}01.$$

	sep.	Δ.	*x*.	*xδ*.
*p‴*1	173·628	3420·32	31¼,	3413·5
	129·272	2532·90	23¼,	2539·7
	302·900	**5953·22**+19·5*dv*	54½	(**109·233**+·36*dv*)
*p‴*2	31·52	3164	29,	3167·7
	22·16	2219	20¼,	2211·9
	53·68	**5383·6**+100*dv*	49¼,	**5379·7**
*p‴*3	9·52	2448	22½,	2457·7
	7·39	1896	17¼,	1884·3
	16·91	**4344**+257*dv*	39½,	**4342·0**
p	44·11	1913·2	17½, 1911·5	*1938·8* *17¾, 1938·8*
	35·87	1551·9	14¼, 1556·6	*1572·7* *14½, 1583·9*
	79·98	**3465·1**+43*dv*−·212ξ	31¾, **3468·1**	**3511·5** *32½,* **3522·7**
d′	14·222	353·88	3¼, 355·0	*357·13* *3¼, 355·0*
	8·703	216·6	2, 218·46	*218·42* *2, 218·46*
	22·925	**570·50**+25*dv*−·025ξ	5¼, **573·46**	**575·55** 5¼, **573·46**

Separations with three decimal places are the means of several good measures. The Δ are slightly affected by errors in the limit, with possible changes in N, as well as in the

separations. In $p'''2$ an exact multiple requires a $d\nu = -\cdot039$. As ν is measured on lines about 3660A, this requires $d\lambda = \cdot005$. In $p'''3$ an exact multiple requires also $d\lambda = \cdot005$. In p' it is curious that both hypotheses give close multiples for ν_1, but the crucial values for $\nu_1+\nu_2$ definitely exclude the S′ hypothesis and allow the S^n provided the limit error is about -8 (see IV. p. 342). The d' numbers as they stand exclude both, although the multiple law is clearly indicated. The valid deduction is that as we are dealing with new types of sequences (the Zeeman patterns * are quite different from those of our known triplets in group II.) we are not justified in assuming *à priori* that rules based on the others are rigorously applicable to these new ones. What the discussion really shows is that the old rules are still applicable rigorously to the main triplet terms and probably with some modification to the new "singlet" triplets. *E. g.*, where the old rule applies to the sum, here, in the narrow triplets it applies to the first, and not to the second, but this question cannot be decided at present. From this point of view it may be interesting to place on record the data determined from the first two of Catalan's multiplets. In both these we have double sets depending on the same p', d' limits with common second terms, say ϕ_1, ϕ_2.... In the first, $\phi_1 = N/(2\cdot9\ldots)^2$ with small separations suggesting analogy with D′′′. The separations adopted are the means of all the observed, and the Δ are discussed for σ_1, $\sigma_1+\sigma_2$.... In the second $\phi_2 = N/(1\cdot59\ldots)^2$, the separations are large and are adopted from the measures of the $p'-\phi_2$ multiplet as they are more reliable than those from $d'-\phi_2$. This term ϕ_2 is important, acting as the limit term in the remaining multiplets.

ϕ_1	σ_1	4·76	535·17	5,	546·1	*547·4*	*5,*	*546·1*
	$\sigma_1+\sigma_2$	8·29	930·1	$8\frac{1}{2}$,	928·5	*953·6*	$8\frac{3}{4}$,	*955·7*
	$\sigma_1\ldots\sigma_3$	10·83	1212·9	11,	1201·6	*1245·9*	$11\frac{1}{2}$,	*1256·1*
	$\sigma_1\ldots\sigma_4$	12·40	1391·28 $+112d\nu$	$11\frac{3}{4}$,	1283·5	*1426·4 +115dν*	*13,*	*1420*
ϕ	σ_1	229·67	$4264+18d\nu$	39,	4260·1	*4297*	$39\frac{1}{4}$,	*4287·4*
	σ_2	169·53	3170	29,	3167·8	*3193*	$29\frac{1}{4}$,	*3195·1*
	σ_3	116·95	2197	20,	2184·7	*2214*	$20\frac{1}{4}$,	*2211·97*
	σ_4	68·64	1294	12,	1310·8	*1304*	*12,*	*1310·8*
	$\sigma_4\ldots\sigma_1$	584·79	10924·8 $+19d\nu-\cdot383\xi$	100,	$10923\cdot3\pm2$	*11007·9*	$100\frac{3}{4}$,	*11005·2±2*

In ϕ_1, σ_4 is mean of 1·62, 1·52, of which the latter is the more reliable. It would make the final Δ 1385·7, *1420·6*.

* Back, *Z. f. Phys.* xv. p. 206 (1923).

The $-\xi$ would increase the former, the latter is exact 13δ within errors.

In ϕ_2 the small coefficient of $d\nu$ makes the conditions more exigeant. The S′ hypothesis here also best satisfies our old conditions, especially when the S^n data are modified by the $-\xi$ condition. There are therefore good grounds for suspecting that the S′ hypothesis is correct and that the new sequences obey the old rules subject to some multiplet modification analogous to the old "triplet."

IV. *Displacement in the Manganese Spectrum.*

We come now to the consideration and discussion of the statement made above that the normal representatives of the S and D triplets for orders of $m=6$ and beyond are disrupted into congeries of displaced lines. For the sake of readers not familiar with this condition it may be convenient to begin with some remarks on displacement in general. When a change takes place in the mantissa of the function $N/(m+\text{mantissa})^2$ which gives the value of a term, the new line is said to be displaced and its wave number is shifted a definite amount. *E. g.*, in Mn, $p_1 1$ is $N/(1{\cdot}630526)^2$. If we deduct a quantity ·003420 from the mantissa, $N/(1{\cdot}627106)^2$ gives $p_2 1$ and p_2 is shifted from p_1 by $\nu_1=173{\cdot}62$. Here the displacement 3420* is $31\frac{1}{4}\delta$ *or* 125 ouns. A further displacement of 2532, or 93 ouns, shifts to p_3 by $\nu_2=129{\cdot}24$. In general—and always in the recognized series—the wave number of a line depends on the difference of two terms, and displacement may occur in each term, giving a line shifted from the original. This for example occurs in diffuse series where the doublet or triplet separations are produced by displacements in the limit p_1, and the satellites by displacements in the $d(m)$ term. In practically all known cases the displacement value is a multiple of the oun. A line displaced from a given one is represented by writing the displacement on the limit (or first term) before the line symbol and that on the sequence or second term after. Thus $D_{22}(m)$ is $(-x\delta)\ D_{11}(m)(-y\delta)$, where $x\delta$ is deducted in p_1—$31\frac{1}{4}\delta$ in the above example—and $y\delta$ is deducted in the d_1. For example, in Mn the line 3547·792 or $D_{22}(2)$ is $(-31\frac{1}{4}\delta)\ D_1(2)(-2\frac{1}{4}\delta)$.

Now it is found that this shifting or production of new lines by displacement is a very common effect and not confined to the multiplets of the generally recognized series.

* It is convenient to treat the mantissa as multiplied by 10^6.

It is especially common in connexion with the higher order of series lines, the actual series lines being either reduced in intensity or absent and replaced by several displaced representatives or "collaterals." The effect may take place when the excitation is produced by the arc, but even more copiously when the spark is employed. It is a common fetish to regard a spectrum produced by a spark as depending wholly on ionized elements with the exception of a few stubborn series lines of the neutral element which have managed to survive. Collaterals are also found in rich arc spectra, but linkages seem to be a special feature of those of the spark. Indeed in the present case the arc spectrum of Mn, as observed by Fritsch, terminates just beyond the S and D limit—*i.e.* extreme limit of displacement—whilst the spark by Exner and Haschek continues very considerably beyond—*i.e.* to link possibilities. It is probable that when a spectrum by the spark is rich in lines, the richness is due largely to the prevalence (1) of collaterals of neutral atomic series lines, and (2) of linkages to individual series lines. Such collaterals are to be looked for in the neighbourhood of the higher series lines, and their existence often enables us to reconstruct the normal series representative, even when it has itself disappeared. They often indicate themselves by showing repeated separations close to those of the normal doublets or triplets. Frequently, also, we find a number of lines close together, separated from one another by amounts which are multiples of some common factor. In such a case they may be suspected to be collaterally related, and if this common factor corresponds to the shift produced by an oun displacement in one of the terms of the series line in question, it is good evidence that they are actually collaterals. It must of course not be forgotten that a single numerical agreement may be a chance coincidence, and must not be regarded as a proof by itself of actual collateral relation.

As in general displacement may occur in two terms, the identification of a single line as such a collateral of another is not easy *. But for our present purpose we are dealing with high order lines, and in this case the shift per oun in the sequence term is exceedingly small, and a small fraction of the observation errors. Consequently any observed shift is almost wholly due to displacement in the limit term alone. If large displacements on the sequence term also occur, the above regularities will not appear, and the collateral would not thus be recognized.

* For some examples see 'Analysis,' p. 139.

We proceed to illustrate the above remarks by a discussion of the observed data in regions corresponding to S (6, 7) and D (5, 6, 7). In doing so, the object is not so much to determine the value of series lines themselves as to give evidence for the displacement effect and to illustrate method. Consequently we shall have to adduce a considerable quantity of data which the application of the method may show to be irrelevant.

For any number of ouns here dealt with, the shift in any case will be very nearly proportional to the number taking part in a displacement. The shifts per oun displacement are 1·3816 in p_1, 1·3911 in p_2, and 1·3968 in p_3. Those for $s\,6$, $d\,5$, $d\,6$, are respectively ·023, ·029, ·018. For the sake of reference the shift multiples up to 12 and for 16, 20, 24 are here given :—

	1.	2.	3.	4.	5.	6.	7.	8.
p_1	1·38	2·76	4·14	5·53	6·91	8·29	9·67	11·05
p_2	1·39	2·78	4·17	5·56	6·95	8·35	9·74	11·13
p_3	1·40	2·79	4·19	5·59	6·98	8·38	9·78	11·17

	9.	10.	11.	12.	16.	20.	24.
p_1	12·43	13·82	15·20	16·58	22·10	27·63	33·16
p_2	12·52	13·91	15·30	16·69	22·26	27·82	33·39
p_3	12·57	13·97	15·36	16·76	22·35	27·94	33·52

Deviation from proportionality for x ouns $= \pm$·0000350 x for $\mp x$, or shift per oun on $(x\delta_1)p =$·0000350 $(2x+1)$.

As the formula gives the exact value for S (5) we may feel confidence in its reliability for higher orders. For S (6, 7) it gives wave numbers 38547·05 and 39233·45. In the following, Fritsch's measures in the arc and those of Exner and Haschek's in the spark are used with wave numbers expressed in I/A. All successive observed lines are taken in each region. The first wave-lengths in each are 2595·847, 2584·432, 2576·284. Separations of successive lines are shown with deviations from oun shifts, the shift per oun being denoted by s. Those accepted as obeying the multiple law are indicated by an asterisk.

In the S_1 set 38541 definitely has no multiple shifts, and indeed the line cannot belong to the S system since it is strongly enhanced in the spark. Of the others we get displacement evidence as between (1, 2, 5) in the arc and (2, 3) in the spark respectively with $18s + ·03$, $12s - ·05$, $10s - ·03$. It should be possible to determine a very accurate estimate of the normal line taking the calculated value as a guide.

	No.	I.	Arc.			I.	Spark.		
S_1	1	5,	38512·85			2,	38497·25		
				24·90	$18s+·03*$			16·90	$12s+·32$
	2	2.	37·75			3,	514·15		
				3·92	$3s-·22$			13·79	$10s-·03*$
	3	4,	41·67			2,	527·94		
				3·13	$2s+·37$				
	4	4,	44·80						
				9·48	$7s-·19$				
	5	5,	54·28						

(5)−(2)=16·53 $12s-·05*$.

S_2	1	4,	38682·95			2,	38703·34		
				2·88	$2s+·10*$			5·40	$4s-·16$
	2	4,	85·83			1,	08·74		
				12·35	$9s-·17$			2·85	$2s+·07*$
	3	3,	98·18			1,	11·59		
				·69				11·09	$8s+·04*$
	4	3,	98·87			1,	22·68		
				1·98					
	5	2,	700·85						
				·88					
	6	1,	01·73						
				19·73	$14s+·28$				
	7	1,	21·48						

(3)−(1)=$11s-·07*$;
(5)−(3)=$2s-·11*$;
(6)−(4)=$2s+·08*$.

S_3	1	5,	38805·28			4 R,	38806·53		
				9·87	$7s+09*$			9·04	
	2	5,	15·15			2,	15·57		
				6·53				19·00	
	3	1,	21·68			1,	34·57		
				3·72				22·03	
	4	1,	25·40			1,	56·60		
				6·23				5·14	
	5	1,	31·63			1,	61·74		
				·77				8·15	
	6	1,	32·40			1,	69·89		
				23·70	$17s-·05*$			14·51	
	7	5,	56·10			2,	84·40		

(5)−(2)=$12s-·28$;
(6)−(4)=$5s+·01*$.

(6)−(2)=$39s-·10*$;
(7)−(4)=$29s-·12$.

Treating the arc lines as displaced 25, 7, −5 ouns on S_1, *i. e.* shifted 34·54, 9·67, 6·91 and the spark as displaced 24, 14 ouns or shifted 33·16, 19·34, we find

arc ... $S_1(6)=38547·39, ·42, ·37$, mean $38547·393 \pm ·023$
spark... ,, = ... 47·31, ·28, ,, $38547·295 \pm ·015$.

The difference between the two means is not larger than that to be expected between the absolute measures of two observers, here Fritsch and Exner and Haschek. The arc mean gives O−C $d\lambda = -·02$.

In S_2 we take (1, 2, 3, 5, 7) in the arc as displaced by 27, 25. 16, 14, −1 ouns giving shifts 37·53, 34·76, 22·26. 19·47

$-1{\cdot}39$ and (1, 2, 3, 4) in the spark by 12, 8, 6, -2 ouns with shifts $16{\cdot}69$, $11{\cdot}13$, $8{\cdot}35$, $-2{\cdot}78$. The results are

arc ... 38720·48, ·59, ·44, ·32, ·09, mean 38720·384
spark ... ... 20·03, 19·87, ·94, ·90, „ 38719·935.

But although these are strikingly mutual limit collaterals they do not give a value of S_2 corresponding to $S_1(6)$. The other set (4, 6), however, do. Regarded as 16, 14 oun displacements or shifted $22{\cdot}26$, $19{\cdot}47$ they give for $S_2(6)$

38721·13, ·20, mean 38721·16; $\nu_1 = 173{\cdot}77$.

The first set correspond to a ·8 shift on the s (6) term, about a 35 δ_1 displacement.

In S_3, (1) in the arc is a greatly enhanced line in the spark (4 R to 30 R) and the agreement in (2) — (1) is probably a chance coincidence. (4, 6, 7), as displaced 18, 13, -4 ouns or shifted $25{\cdot}14$, $18{\cdot}14$, $-5{\cdot}59$ give 38850·54, ·54, ·51, mean 38850·53, with $\nu_2 = 129{\cdot}37$, in good agreement. The spark measures definitely exclude the enhanced line, and it is remarkable that out of the 15 possible combinations of the other six spark lines only two sets show a multiple connexion accepted only because the observation errors in the spark are larger. The arc lines (2, 5) with 25, 13 ouns and shifts $34{\cdot}90$, $18{\cdot}16$ and the spark (2, 6) with 25, -14 ouns and shifts $34{\cdot}90$, $-19{\cdot}56$ give

arc ... 38850·05, 49·79, mean 38849·92
spark ... ... 50·47, ·33, „ 38850·40.

The spark may correspond to the former arc set. The arc set here give $\nu_2 = 128{\cdot}76$, and they correspond therefore to lines also displaced about 24 ouns in s (6) (shift = ·51).

The final results for the S(6) triplets are thus:

38547·39
173·77
38721·16
129·37
38850·53

The fact that with so large a factor as 1·4 we get such close agreement in so many cases is very striking.

In further support of the displacement effect we may notice the following sets with triplet separations.

A.	B.	C.	D.	E.
38512·85	38554·28	38527·94 *s*		38537·75
172·98	**173·66**	**172·91**		**173·84**
635·83	727·94	700·85	38701·73	711·59 *s*
129·32	**128·68**	**130·78**	**130·67**	**172·81**
815·15	856·62	831·63	832·40	884·40 *s*

These illustrate the fact that where doublets or triplets are disrupted into collaterals we find a considerable number of sets in the neighbourhood with separations nearly, but not the same as the normal ones. Here

A is Catalan's suggestion for S(6). It is the set $(25\,\delta_1)\,S\,(6)$ with O−C $d\lambda = -\cdot 02$. The displacement of 25 ouns requires a diminution of $\nu_1+\nu_2$ by ·38 to 302·48. The observed 302·30 is within observation errors of this.

B is $(-6\delta_1)\,S(6)$: O−C $d\lambda$ on $S_1=0$.

C. The first two form the set suggested in the 'Analysis.' They are $(7\,\delta_1)\,S_{1,2}(6)$.

The calculated values for D(5, 6, 7) are 38097·29, 38947·73, 39495·44. In the region of D_1 there are few spark lines, and these represented in the arc. There is a gap in the arc lines after 38300, whilst the spark is rich. Consequently for $m=5$ we take arc lines for D_1 and spark for D_3. The calculated D_1 is directly observed at 38097·37. The separations from this—or corresponding D_2, D_3—are entered in the list with the multiple deviations. The first wave-lengths in each region are 2625·226, 2613·669, 2604·44.

	$D_1(5)$ arc.			$D_2(5)$ arc.		
1	2,	38081·88	$11\,s+\cdot 29$	2,	38250·27	$15\,s-\cdot 14$ *
2	4,	86·52	$8\,s-\cdot 20$	4,	60·95	$7\,s+\cdot 30$
3	1,	88·20	$7\,s-\cdot 50$	1,	65·03	$4\,s+\cdot 40$
4	4,	97·37	0 *	4,	300·23	$-21\,s-\cdot 03$ *
5	4,	108·41	$-\,8\,s+\cdot 01$ *			
6	5,	14·02	$-12\,s-\cdot 07$ *	(3)−(2)=	4·08=	$3\,s-\cdot 09$ *
7	1,	37·45	$-29\,s-\cdot 01$ *	(5)−(1)=	49·96=	$36\,s-\cdot 08$ *
	$D_2(5)$ spark.			$D_3(5)$ spark.		
1	1,	38243·52	$20\,s-\cdot 35$	2,	38385·80	$10\,s+\cdot 46$
2	1,	64·15	$5\,s-\cdot 11$ *		87·91 †	$9\,s-\cdot 25$
3	1,	90·08	$-14\,s+\cdot 38$	3,	95·09	$4\,s-\cdot 44$
4	1,	94·04	$-17\,s+\cdot 60$	1,	402·60	$-2\,s+\cdot 42$
5	1.	300·20	$-21\,s+0$ *	1,	03·80 §	$-3\,s-\cdot 62$
6	2,	09·30	$-28\,s+\cdot 64$	1,	04·52	$-3\,s-\cdot 10$ *
7				3,	09·68	$-7\,s+\cdot 33$
8				1,	18·39	$-13\,s+0$ *
(6)−(4)=	15·26=	$11\,s-\cdot 04$ *.		(7)−(4)=	7·08=	$5\,s+\cdot 10$ *.

† Corrected from Catalan's ...89·4. § Arc.

In D_1 (4, 5, 6, 7) give $D_1 5$ = mean of 38097·37, ·36, ·44, ·37 = 38097·387. For D_2, 38300 arc and spark is enhanced and

had best be excluded. In the arc (3, 2) require also displ. in $d(5)$ (of about ·35), as also 6, 4 in the spark (of about ·6). (2) in spark is good. It gives $D_2 5 = 38271{\cdot}10$. $D_3 5$ from (6, 8) is mean of 38400·33, ·23 = 38400·280.

The D (5) set is thus

38097·387 O−C $d\lambda = -{\cdot}007$

173·71

38271·10 302·89

129·18

38400·280

Here the ν_1, ν_2 are practically exact normal separations. Amongst the above are

$(8\delta_1)$ D, 38086·52 $(-12\delta_1)$ D, 38114·02 38265·03

174·43 129·50 130·06

260·95 301·39 243·52 395·09

126·96

387·91

The first set is Catalan's allocation for D(5), but the separations are abnormal. For a set $(8\delta_1)$D the triplet separations should be 173·54, 129·20, sum 302·74. The deviations are greater than can be accounted for by observation errors and must be due to displacements in $d(5)$.

The lines for S(7), D(6, 7) and beyond become intermixed. The number of spark lines is so large that we will omit their consideration except where absence of collaterals appear amongst those of the arc. Take the arc lines from 2567·529 to 2527·539.

	1	1,	38937·60	10·13			
$D_1 6$							
	2	2,	55·51	− 7·78			
	3	3,	58·67	−10·94,	− 8 s + ·11		
	4	2,	59·51	−11·78			
	5	2,	70·86	−23·13,	−17 s + ·36		
	6	3,	94·66†				
	7	2,	39001·32	−53·59,	−39 s + ·35		
	8	2,	59·31	62·04,	45 s − ·49		
	9	3,	98·52	22·83			
	10	1,	102·32	19·03,	14 s − ·44		
$D_2 6$							
	11	1,	40·89	−19·54,	−14 s − ·07		
	12	4,	222·52				
$S_1 7$, $D_3 6$							
	13	2,	39255·83				
	14	1,	312·75				
	15	3,	14·45				
	16	3,	18·88				
	17	4,	25·24				
	18	1,	62·12				
	19	3,	63·91				
	20	3,	67·88				
$S_2 7$							
	21	4,	465·79				
$D_1 7$							
	22	1,	68·67				
	23	4,	502·71				
$S_2 7$							
	24	5,	53·62				

† Enhanced line.

Taking first (1 ... 7), as in the region of $D_1(6)$, the numbers entered on the right are separations from the calculated

$D_1(6)$. (3) as $(-2\delta)D_1(6)$ gives $D_1(6)=38947{\cdot}62$, O−C $d\lambda=\cdot007$. (5, 7)—separation $=22s+\cdot01*$ have the same d sequence but probably displaced from the normal $d(6)$. Also (1, 2, 4?) separated by 17·91, 4·00, or $4s-\cdot05*$, $3s-\cdot14$ (?*) are possible mutual limit collaterals, displaced also by the same amount in their d terms.

(8...11) are in the $D_2(6)$ region. Of these (8, 10) are relatively shifted by $31s-\cdot05*$. (11) as $(-14\delta_1)D_2(6)$ gives $D_2(6)=39140{\cdot}89-19{\cdot}47=39121{\cdot}42$. It and (10) will be equally and oppositely displaced $\pm14\delta_1$ in the limit, and (10) in addition by a small one in d.

The four or more lines beyond (12) are in the neighbourhood of $S_1(7)$ and $D_3(6)$. These both lie between (12) and (13). These are separated by 33·31 which is $24s+\cdot15$ if both are related to S_1 and $24s-\cdot20$ if to D_3. They cannot therefore be mutual limit collaterals. The smallest displacements would suggest allocating (12) to S_1 and (13) to D_3, but this is no necessary condition, and indeed if (12) be a D_3 line it gives a correct $\nu_1+\nu_2$ with the D_1 determined above. Thus (12) as displaced $20\delta_1$ gives $D_3(6)=39222{\cdot}52+27{\cdot}92=39250{\cdot}44$ and the whole set give $\nu_1=173{\cdot}80$, $\nu_2=129{\cdot}02$, $\nu_1+\nu_2=302{\cdot}82$.

In this case (13) cannot be a limit displacement of D_3, but if it is connected with $S_1(7)$ it is displaced $-16\delta_1$ and gives $S_1(7)=39255{\cdot}83-22{\cdot}11=39233{\cdot}72$ with O−C $d\lambda=-\cdot02$. But there is little supporting evidence for the allocation.

$S_2(7)$ comes between (20, 21) and $D_1(7)$ between (21, 22). The separations of (20, 21) from the calculated S_2 are 39·19 $=28s+\cdot27$ and $-58{\cdot}72=-42s-\cdot22$. Their mutual separation is thus $70s+\cdot49$ so that they cannot be mutual limit collaterals. (20) as $(28\delta_1)S_2$ gives $S_27=39367{\cdot}88+38{\cdot}92=39406{\cdot}80$, O−C $d\lambda=-\cdot017$. $S_3(7)$ comes between (23, 24), separated by $50{\cdot}91=36s+\cdot62$, and consequently not mutual limit collaterals. (23) as $(24\delta_1)S_3$ gives $S_3(7)=39502{\cdot}71+33{\cdot}50=39536{\cdot}21$, O−C $d\lambda=\cdot006$. The absence of collaterals in the arc lines for the S(7) set, however, renders the evidence precarious as it depends only on a general agreement with formulæ values. In its favour is the fact that the resulting ν_2 separation $129{\cdot}41=\nu_2+\cdot17$ is good, although the ν_1, $172{\cdot}08=\nu_1-\cdot54$, is bad. There are few arc lines in the neighbourhood although the spark are numerous, but not so well measured. *E.g.* the spark lines λλ2537·45, 2536·91 or nn.39399·13, 39407·52, separated by $8{\cdot}39=6s+\cdot05$ for S_1, are mutual limit collaterals, and, as $(6\delta_1)S_2$ and S_2 give $39399{\cdot}13+8{\cdot}35=39407{\cdot}48$ and ...07·52, mean 39407·50, close to the calculated ...07·07. We should not

expect the normal S_2 to appear in the spark and not in the arc. This is therefore probably not the true $S_2(7)$, but the two are displaced by the same amount in the $s(7)$ term.

(21, 22) are separated by $2{\cdot}88 = 2s - {\cdot}12$ and may possibly be mutual limit collaterals. Regarded as displaced by $22\delta_1$ and $20\delta_1$ they give for $D_1(7)$ $39465{\cdot}79 + 30{\cdot}40 = \ldots 96{\cdot}19$ and $\ldots 68{\cdot}67 + 27{\cdot}64 = \ldots 96{\cdot}31$, mean $D_1(7) = 39496{\cdot}25$ $O - C\, d\lambda = -{\cdot}05$.

There are no arc lines in the $D_{2,3}(7)$ regions. The series lines here require the spark for collaterals, and these give evidence for displacement. *E. g.*, for these regions, beginning at $\lambda = 2521{\cdot}77$ and $\lambda = 2514{\cdot}75$, we find

	D_2.		D_3.
1	1, 39644·10	1,	39754·76
2	1, 52·28	2,	61·72
3	2, 61·40	2,	817·29
4	1, 66·28	1,	34·10
5	1, 68·49		
6	2, 99·16		

In the first column two different sets satisfy the conditions of mutual displacement, viz. (1, 2, 4) with separations $6s - {\cdot}17$? $10s - {\cdot}09$, and (3, 5, 6) with $5s + {\cdot}13$, $22s + {\cdot}05$. (5) is very near to $D_2 7$, but we should not expect the spark to produce a series line when the arc does not; so that it probably belongs to another series line. Indeed they satisfy $S_1(8)$ which is given by the formula as 39688·16. Taking (1, 2, 4) as 18, 12, 2 ouns on $D_2 7$ and 6 as -8 on $S_1(8)$ gives

$D_2 7 = 39669{\cdot}14$, 8·97, 9·06, mean 69·056, $O - C\, d\lambda = -{\cdot}001$,
$S_1 8 = 39699{\cdot}19 - 11{\cdot}05 = \ldots 88{\cdot}14$.

In the right-hand column there are again two sets of mutual collaterals (1, 2) and (3, 4) with $5s - {\cdot}02$, and $12s + {\cdot}05$ on the $p_3 1$. The first two as 31 and 26 ouns on D_3 give for $D_3(7)$

39798·04, 02, mean 39798·03, $O - C\, d\lambda = {\cdot}015$.

The foregoing discussion gives evidence of the existence of displaced series lines as a general phenomenon. The actual suggestions for individual series lines in $S(m)$, $D(m)$, cannot be proved to be correct owing to the existence of displacement on the current $s(m)$, $d(m)$ sequences, but it is noticeable how closely they reproduce the independent series separations ν_1, ν_2 and how closely they conform to values calculated from the formulæ, of which the S formula has been shown to reproduce one undoubted set with exactness.

The results of the discussion are here collected :—

	6.		7.		8.
S	38547·39		39233·72		39688·14
		173·77		173·08	
	38721·16		39406·80		
		129·37		129·41	
	38850·53		39536·21		

	5.		6		7.	
D	38097·39		38947·62		39496·25 ?	
		173·71		173·80		172·81
	38271·10		39121·42		39669·06	
		129·18		129·02		128·97
	38400·28		39250·44		39798·03	

The wave-lengths of the various lines involved are appended. The figures in brackets denote the number of ouns the limit must be displaced to produce the series line. Thus $(-25)2595, = S_1(6)$ *or* 2595 is $(25\delta_1)\ S_1(6)$. The numbers on the left of a line give the intensity. The measures are in R.A.

$S_1(6)$. Arc 5, (−25)2595·847 ; 2, (−7)...4·170 ; 5, (5)3·057.
Spk. 3, (−24)...95·76 ; 2, (−14)...4·83.

$S_2(6)$. „ 3, (−24)2583·369 ; 1, (−14)...3·178.
Spk. 2, (−12)...3·07 ; 1, (−8)...2·71 ; 1, (−6)...2·52 ; 1, (2)...1·78.

$S_3(6)$. „ 5, (−25)2575·629 ; 1, (−13)...4·536.
Spk. 1, (−25)...5·60 ; 1, (14)...2·00.

$S_1(7)$. 2, (16)2546·713. $S_2(7)$. 3, (−28)...39·465. $S_3(7)$. 4, (−24)...30·797.

$S_1(8)$. 2, (8)2518·27.

$D_1(5)$. 4, 2624·158 ; 4, (8)...3·368 ; 5, (12)...3·011 ; 1, (29)...21·40 *s*.

$D_2(5)$. 1, (−5)2612·72 ; 1, (−20)...4·13 ; 1, (14)...0·95.

$D_3(5)$. 1, (3)2603·17 ; 1, (13)...2·23.

$D_1(6)$. 3, (2)2566·140. $D_2(6)$. 1, (14)...54·193. $D_3(6)$. 4,(−20)...48·877.

$D_1(7)$. 4, (−22)2533·165 ; 1, (−20)...2·980.

$D_2(7)$. 1, (−18)2521·77 ; 1, (−12)...1·25 ; 1, (−2)...0·36.

$D_3(7)$. 1, (−31)2514·75 ; 2, (−26)...4·31.

$S_2(6)(-30\delta_1\pm)$. 4, (−27)2584·432 ; 4, (−25)...4·240 ; 3, (−16)...3·415 ; 2, (−14)...3·237 ; 1, (1)...1·860. Arc.

We now turn to the consideration of the nature of the two parallel narrow triplets. We will denote their formulæ by $p-\phi m$, $d-\phi m$, the question being whether the p is a singlet limit and thus determined indirectly without reference to the series itself, or whether the series is to be regarded as independent and p directly determined from it. We are to test this by examining which of the formulæ is the better supported by the observed data. The series lines themselves will be denoted by S′, D′ or S^n, D^n, the dash referring to singlet and n to narrow series and D to the limit d. The two formulæ give for $m=4$

$$S^n = 18868{\cdot}53, \qquad S' = 18784{\cdot}95,$$
$$D^n = 29836{\cdot}28, \qquad D' = 29752{\cdot}70.$$

The separations are $\nu_1 = 44{\cdot}11$, $\nu_2 = 35{\cdot}87$, $\sigma_1 = 14{\cdot}22$, $\sigma_2 = 8{\cdot}70$. The wave-numbers of the lines observed in these neighbourhoods are given in the two lists below, beginning with $\lambda = 5331{\cdot}479$ and $\lambda = 3366{\cdot}361$ respectively.

List S.

	1	1,	18751·61					$(\Delta_1+2\Delta_2)X_1$
				33·80				
·620	2		85·41†				S_1'	$(\Delta_1+\Delta_2)X_1$
·626				27·93	$45s = 28{\cdot}16$,	*7·92**		
	3	1*n*,	18813·34					$b\,.\,(15\delta_1)X_1$
				1·73				
	4	1*n*,	15·07					
				5·39	$9s = 5{\cdot}64$,	*·60*		
	5	1*n*,	20·46					
				1·76	$3s = 1{\cdot}88$,	*·86*		
·627	6	1*n*,	22·22				$b\,.(-3\delta_1)S_3'$	$b\,.(\delta_1)X_1$
				8·85	$14s = 8{\cdot}78$*,	*·71*		
·622	7	3*n*,	31·07				$(-2\delta_1)S_2'$; $\nu_2\,.\,X_1$ or $b\,.\,(\Delta_2)X_2$	
				35·88				
·629	8	3*n*,	66·95				$(-2\delta_1)S_3'$	X_1 and $b\ X_2$
				3·15	$5s = 3{\cdot}143$*,	*·117*		
	9	2*n*,	70·10					$(-5\delta_1)X_1$
				17·78	$38s = 17{\cdot}62$,	*·46*		
	10	1,	87·88				$(-\Delta_2+22\delta_1)S_3'$	$b(6\delta)X_3$
				12·52	$20s = 12{\cdot}60$*,	*·56**		
	11	2*n*,	18900·40				$(-\Delta_2+2\delta_1)S_3'$	$b(\delta)X_3$
				1·95	$3s = 1{\cdot}89$*,	*·87**		
·625	12	1,	02·35				$(-\Delta_2-\delta_1)S_3'$	$b\,.\,(\delta_1)X_3$
·630				35·40				
·626	13	1,	37·75				$(-2\Delta_2)S_3'$	$b\,.(-\Delta_2+2\delta_1)X_3$
				17·19	$27s = 17{\cdot}06$,	*6·91*		
·632	14	1,	54·94					

(12)−(10) = 14·47 $23s = 14{\cdot}49$*, *·37*
(6)−(3) = 8·88 $14s = 8{\cdot}88$*, *·7*

† Rowland in sun.

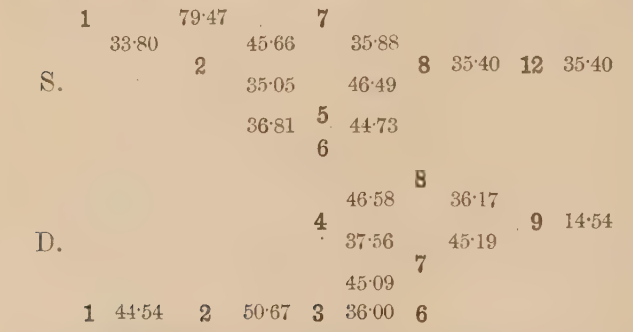
List D.

1,	29698·14			1
	44·54			
3,	742·68		$(10\delta_1)D_1'$	2
	50·67			
1,	93·35		$a\,.(-3\delta_1)D_1^{\,n}$	3
	7·53			
2,	800·88		$b\,.(-10\delta_1)D_1^{\,n}$	4
	26·13			
2,	27·01			5
	2·34			
1,	29·35†			6
	9·09			
2,	38·44		$(-\delta)D_1^{\,n}$	7
	9·02			
3,	47·46			8
	36·17			
2,	83·63		$(-5\delta_1)D_1^{\,n}\,.\,b$	9
	14·54			
3,	98·17		$(-5\delta_1)D_2^{\,n}d$	10

† Exner and Haschek.

These are all the lines observed by Fritsch in the S(4), D(4) regions together with (6) in list D by Exner and Haschek and (2) in List S. The latter is taken from Kayser's *Handbuch* as observed by Rowland in the sun. It has not been observed in the arc or spark by Hasselberg, Fritsch, Kilby, Fuchs, or King. It practically corresponds to the calculated S′(4) and is the only line in the neighbourhood. The question of its reality is therefore crucial as regards the singlet hypothesis. There is no corresponding line for D′(4). The calculated $S^n(4)$ comes half-way between (8, 9), whilst in list, D, (7) is 10967 ahead and is $D^n(4)$.

The first thing to be noticed is the large number of separations close to those of the S triplets. They are shown in the subjoined diagrams, which recall at once the meshes and chains of a linkage system. The figures in thick type refer to the numbered lines in the list. This repetition is a



striking characteristic in many spectra and is a certain sign of multiple displacement, or linkage. Here, in the second list where displacement can only occur in d or ϕ_1, the appearance of p separations cannot be due to displacement, and their presence here points to the linkage effect. In the first list their appearance may be due either to links, or displacement, or both.

We will now examine in more detail the data in the first list. The shifts per δ ($=4\delta_1$) will be slightly different on the two hypotheses, viz. 2·5150 for p^n and *2·4818* for p'—the first near S_1^n at (8) and the second near S_1' at (2). The changes in these after a displacement of $x\delta$ are practically the same, viz. ·000194$(2x+1)$. The shifts per oun are printed on the left of the wave-number, those due to p' being in italics, on the supposition that no linkages enter. The shifts per oun in d_1 are 1·0971 and *1·0871*. The shift per oun in ϕ^n (4) is ·0679 and in $\phi'(4)$ is *·0655*. The successive

separations are given in the column next the wave-number and are followed by the nearest oun shifts on the two hypotheses. It will be seen that the independent hypothesis gives the best agreement. The separation 1·7, which appears twice, cannot be due to limit shifts alone. If due to displacement in ϕ alone, 26 ouns shift 1·76 or *1·70*.

First consider the data on the basis of S^n. The calculated value comes just half-way between (8) and (9), which are definitely mutual limit collaterals of five ouns. The line (9) is separated from (7) in the second list by 10967·75 + ·59. As ·59 is within error limits of ·62 it is natural to take the (7) as the representative of $D^n(4)$ and the (9) as too small by ·62; in other words it represents $(\delta_1)S_1^n(4)$. But as (8) is the stronger line with numerous links, it will be better to take it as our starting point and denote it by X_1, with a limit near p_1^n. Then (9) is $(-5\delta_1)X_1$. (6) is 44·73 behind (8). *If* this is a linkage, the link is $b + ·62$ ($b = \nu_1$) and the line $b\,.\,(\delta_1)X_1$. Now a $(-b)$ link would bring X_1 back ν_1, X_2 to coincide with X_1 and X_3 to a line $\nu_2 = 35·87$ ahead of X_1. We find a line (12) $35·40 = \nu_2 - ·47$ ahead, but ·47 is no oun shift. But if X_3 be linked back by the *a* link instead of the *b*, it should be 35·99 ahead $= 35·40 + ·59$, the ·59 being within reach of an oun shift. But this seems artificial, and it is more probable that displacement occurs in ϕ. Consequently (12) is entered as $b(\delta_1)X_3$, X_3 being regarded as suffering a small displacement in ϕ of two or three ouns. Thus (6 . 8 . 12) give a triplet linked back by *b* from (8). Although this bodily shift of the triplet is exact we do not expect to find, especially in an arc-excited spectrum, that the normal lines wholly disappear when linked. But we have just seen that (8) may be both S_1 and $b\,.\,S_2$, since the two are necessarily the same. In this case the normal S_2, S_3 have disappeared. There is a great deal to be said therefore for this allocation. (7) is an exact ν_2 behind (8) and it would appear as the linked line $\nu_2\,.\,X_1$, but we have no evidence in other spectra of ν_2 acting as a link. If it is $(\Delta_2)X_1$, the separation would be 35·56 and not permissible without concurrent displacement in $\phi(4)$. But (8) is, as shown above, also $b\,.\,X_2$ and $(\Delta_2)X_2$ produces a shift close to the observed 35·88, or (7) is $b\,.\,(\Delta_2)X_2$, and is entered thus.

(13) is 35·40 ahead of (12). A displacement $-\Delta_2$ on X_3 in (12) shifts 35·97, or $35·40 + ·57$, *i.e.* an additional δ_1. The line is $b\,.\,(-\Delta_2 + 2\delta_1)X_3$.

(13, 14) are not mutual collaterals and (14) remains undetermined.

(10, 11) are mutual collaterals with (12) and are therefore $b\,.\,(\delta)X_3$ and $b(6\delta)X_3$.

(1) is 79·46 behind (7). If linked by $\nu_1+\nu_2$ it is ·42 in defect; if displaced $\Delta_1+\Delta_2$, the shift is 79·64 or ·18 in defect. It is numerically $(\Delta_1+2\Delta_2)X_1$, as if (7) were $(\Delta_2)X_1$.

The uncertain line (2) by Rowland is 79·52 behind (8). A displacement of $\Delta_1+\Delta_2$ on p_1 gives 79·64, the same within error limits of the two different observers.

(3) is a 14 oun shift on (6). It is $b\,.\,(15\delta_1)X_1$.

Even if not correct in all details, the foregoing discussion affords strong evidence of a linked and displaced congeries of lines based on the line (8), which we have denoted by X_1.

What is the relation of X_1 to S_1^n? The system is clearly built on X_1. We have the triplet set $b\,.\,(\delta_1)X_1$, X_1 or $b\,.\,X_2$, and $b\,.\,(\delta_1)X_3$, or say if $X_1=(-\delta_1)S_1^n$ the set $b\,.\,S_1$, $b\,.\,(-\delta_1)S_2$. $b\,.\,S_3$. Now the line 29838·44, which is 10968·34 $=10967\cdot75+\cdot59$ from (9) would seem to point to (9) with a δ_1 displacement as the true S_1. But there may be displacement on the line 29838 as well. If X_1 is true S_1 the true D_1 is 29834·68; whereas if $X_1=(-\delta_1)S_1$ the true S_1 is 18166·30 and the true $D_1=29834\cdot05$. These are respectively 3·76 and 4·39 behind the observed line. The shift per oun is here 1·0971, of which 3·76 is no multiple, whilst a 4 oun or δ shift is 4·388 or exact. Thus the combined evidence points to 18166·30 as the true $S_1^n(4)$ and 29838·44 is $(-\delta)D_1^n(4)$. This gives the O − C error of the calculated S_1 as $dn=-2\cdot23$ or $d\lambda=\cdot62$. This can be explained by the limit having been taken too large by a few units—easily the case, since it was determined by using the first three lines of the series. We should then expect to find that the calculated $S_1 5$ should be in excess by a quantity greater than 2. Indeed, if the formula be calculated from $m=2$, 3 and this for $m=4$, the limit is 5·75 less and the calculated for $m=5$ is 20719·19.

When we now proceed to test the data on the supposition that (2) is near the true S_1' we have the uncertainty as to the relative separations due to the fact that (2) is due to a different observer. *E. g.*, if it is correct, (3) is an exact limit collateral, but in the triplet (2 . 7 . 8) whilst ν_2 is correct the $\nu_1=45\cdot66$ is 1·55 in excess and cannot be a pure displacement (1·55 = 2 oun shifts + ·32). Since we have here an otherwise good triplet we shall take the ·32 as an obs. error, in which case (3) must be taken as not a limit displacement of (2), and 7, 8 become $(-2\delta_1)S_2'$, $(-2\delta_1)S_3'$.

(12) is 35·40 ahead of (8). An additional Δ_2 displacement shifts 35·96 or ·56 too large, ·61 being equivalent to an additional δ_1. Thus (12) is $(-\Delta_2-\delta_1)S_3$. (10, 11) are related to 12, as in the former case.

(13) is 35·40 ahead of (12), *i. e.* of $(-\Delta_2-\delta_1)S_3'$. An extra Δ_2 displacement shifts 36·03, requiring ·63 less or $+\delta_1$ on the limit. It is therefore $(-2\Delta_2)S'_3$.

(6) is $44{\cdot}73=\nu_1+{\cdot}62$ behind (8). If linked, it requires also δ_1 on the limit and is $b\,.\,(-3\delta_1)S'_3$; if displaced $-\Delta_1$ on the S_3 it shifts 44·23 or ·50 too little. The former is therefore adopted. It will be seen that both the S', S^n hypotheses work in well with linked and displaced lines. The S^n show more definitely small displacements, but are weak in explaining the exact ν_2 at (7, 8). The S' theory has to impose a definite obs. error on one line. It then forms a well-connected system, with a definite triplet; but it is difficult to explain why what should be the strongest line thereof has not been observed directly in the laboratory. The failure to discriminate between the two theories is due to two causes :—(1) the appearance of links, these being independent of the line origins; (2) the coincidence that the calculated S_1' and S_1^n are separated about $\nu_1+\nu_2$, so that one comes at the beginning of a triplet and the other at the end.

The parallel D′ would be at 29753·48 if $(2)+{\cdot}32=S'$. The nearest observed line is 29742·68 at (2) in the second list. It is separated from the supposed D_1' by 10·80 or $10s-{\cdot}07$, so that (2) may be related by displacement on the limit alone.

The D list contains the lines from $\lambda=3366{\cdot}361$. The shifts per oun on the limit are 1·0971 for D_1^n and *1·0858* for D_1'. These lines are quite beyond the reach of any series with a p_1 limit. The appearance therefore of a large number of separations near the ν_1, ν_2 of that limit (see D diagram above) can only be accounted for by their entrance as links. We have taken (7) as $(-\delta)D_1^n(4)$.

(9) is $45{\cdot}19=\nu_1+1{\cdot}08$ ahead, *i. e.* a b link and a δ_1 displacement or d_1. It is therefore $(-5\delta_1)D_1^u.b$.

(10) is 14·54 or $\sigma_1+{\cdot}32$ ahead, where σ_1 is the D separation 14·22 and cannot serve. But as a d link (44·36) to (7) it gives $44{\cdot}36+14{\cdot}22+1{\cdot}097=59{\cdot}68$ to meet the observed 59·73. Hence it is $(-5\delta_1)D_2^n.d$.

(3) is 45·09 behind (7). The a link is 43·99, and a δ_1 shift gives 45·09 exact. It is therefore $a\,.\,(-3\delta_1)D_1^a$.

(4) is 7·53 ahead of (3). $12\delta_1$ on p_1 shifts 7·545; $7\delta_1$ on d_1 shifts 7·68. As p_1 occurs in the a link of (3) the $12\delta_1$

shift might be thus accounted for, but we have no experience in this connexion. The $7\delta_1$ shift is 7·60 on d_1' and would fit, but we have found no other d' relations. The $7\delta_1$ shift $=7{\cdot}68$ on d^n is excessive, but it fits to a previous b instead of a (shift 7·65). It is thus $b(-10\delta_1)\mathrm{D}_1{}^n$.

The appearance of the separations 36 involves in both cases the explanation for the two separations 9·0. Clearly ϕ displacements are involved. We need not extend the discussion. The important point for our present purpose is not a true allocation, but the fact that a consistent allocation is possible on established lines involving both D_1 and D_2 provided the triplet system is an independent one.

For $m=5$ the formulæ give $\mathrm{S}_1{}^n(5)=20722{\cdot}76$, $\mathrm{S}_1{}'(5)=20589{\cdot}40$ with the oun shift on $\phi(5)={\cdot}0355$. The list, starting from $\lambda=4862{\cdot}261$, is long, so as to include the regions round both S' and S^n, which are now much farther apart than in $m=4$. Again we find the excess of separations near ν_1, ν_2 (see diagram), and at the same time a large number of oun shifts *. It is to be noticed that (16) shows none of these. This is as it should be since (16) is $\mathrm{S}_1{}'''(2)$, where the oun shift is 1·38. Further, none of the other lines show multiples of this 1·38, in other words no limit displacements of $\mathrm{S}_1{}'''(2)$ occur. This also is in accordance with experience, as the lower orders of a series are little subject to this effect. It will be seen that the multiple shifts, as shown, afford little discrimination between the two hypotheses, since where the larger separations occur, both hypotheses exclude them. There is a possible exception with $(13)-(12)=8{\cdot}68$, but here (13) is by a different observer.

On the S^n hypothesis, the calculated $\mathrm{S}_1(5)$ falls between (15, 16), but from the discussion on S(4) we were led to expect a somewhat smaller value. In fact the evidence at once points to (14) as close to the true S_1 because it has a ν_1 forward, is the centre of numerous links, and especially because there is a line, (7) list D, $10966{\cdot}82=\mathrm{C}-{\cdot}93$, ahead to represent $\mathrm{D}_1(5)$. The defect ·93 cannot be explained by a displacement on one line only. But if the two observed lines be $(2\delta_1)\mathrm{S}_1$ and $(2\delta_1)\mathrm{D}_1$, the separation of $\mathrm{D}_1, \mathrm{S}_1 = 31678{\cdot}23+2{\cdot}194-(20711{\cdot}41+1{\cdot}257)=10967{\cdot}757$, the true C. We shall take then (14) as $(2\delta_1)\mathrm{S}_1$.

* These are calculated as on lines wholly displaced from the initial line. They will be modified where links enter.

S.

1	4,	20561·53	15·09	$24s$=14·98*,	·33	
2	3,	76·62	2·81			
3	3,	79·43	4·12			
4	3,	83·55				
5	2,	84·46,	8·74	$14s$= 8·75*,	·68	$(13\delta_1)S_1'$
6	2,	92·29	·79			
7	3,	93·08	25·87	$41s$=25·65,	·44	$(-\delta_1)S_1''$; *a* . *b* . $(50\delta_1)S_1^n$
8	3,	20618·95	17·86	$29s$=18·14,	·00	*a* . *b* . $(9\delta_1)S_1^n$
9	4,	36·81	14·96	$24s$=15·03*,	4·99*	S_1' . *d*
10	2,	44·57,				
11	3,	51·77	2·47	$4s$= 2·51*,	·49*	*b* . $(27\delta_1)S_1^n$
12	3,	54·24	8·68	$14s$= 8·78*,	·71*	*b* . $(23\delta_1)S_1^n$
13	2,	62·92†	48·49			*b* . $(9\delta_1)S_1^n$
14	3,	20711·41	5·59	$9s$= 5·66*,	·62*	$(2\delta_1)S_1^n$
15	4,	17·00				$(-7\delta_1)S_1^n$
16	6‖,	25·95§	9·66			
17	3,	26·66	21·71			
18	1,	48·37	5·88	$9s$= 5·67,	·63	$(-\Delta_2)S_1^n$
19	1,	54·25	42·08			$(\delta)S_2^n$
20	2,	96·33	2·86			$(-6\delta_1)S_3^n$
21	2,	99·19				$(3\delta_1)S_3^n$. *d*

† Kilby only. § is $S_1''(2)$.

D.

1		31564·69†	$(3\delta_1)D_1'$			
2						
3	4,	31625·58§				
4	2,	34·58	*a* . $(2\delta_1)D_1^n$?			
5	2,	36·80	*a* . D_1^n?			
6	1,	48·73	*a* . $(2\delta_1)D_2^n$?			
7	1,	78·23	$(2\delta_1)D_2^n$			
8	1,	31737·22 ‖	$(2\delta_1)D_2^n$. *d*			
9	3,	48·29	47·75	D_3^n . *d*		

Diagram.

† Rowland in sun.
§ $S_2''(3)$.
‖ E.H.

(19) is $42{\cdot}84=\nu_1-1{\cdot}27$ ahead and $2\delta_1$ shifts 1·26; it is therefore $(\delta)S_2$.

(21) is $44{\cdot}94=\nu_1+{\cdot}83=d+{\cdot}58$ ahead of the last, where the d link is 44·36. It is therefore $(3\delta_1)S_2\,.\,d$.

(18) is 36·96 ahead of (14). $A-\Delta_2$ displacement on p_1 shifts 35·70 and the excess is now 1·26 or a two oun shift. It is therefore $(-\Delta_2)S_1$.

(13) is $48{\cdot}49=\nu_1+4{\cdot}38$ behind (14) and $7\delta_1$ shifts 4·40. Thus we have a b link back and $7\delta_1$ on limit, or the line is $b\,.\,(9\delta_1)S_1$. *or* since another observer is here involved it may be $(\Delta_1+9\delta_1)S_1$.

(13, 12, 11, 9) are mutually displaced as shown in the list, *i.e.* they are respectively $b\,.\,[23\delta_1, 27\delta_1, 51\delta_1]S_1$. As $\Delta_2=57\delta_1$ the last may be written $b\,.(\Delta_2-6\delta_1)S_1$.

(8) is 43·97 behind (13). The separation is practically the exact link $a=43{\cdot}99$. It is therefore $a\,.\,b\,.\,(9\delta_1)S_1$.

(7) is shown as $41s-{\cdot}22$ behind (8). But if (8) is as just determined, the shift is directly on S_1 and then $41s=25{\cdot}79*$. Thus (7) is $a\,.\,b(50\delta_1)S_1$.

(5) is 8·62 behind, and the oun shift on $(50\delta_1)S_1$ is ·6270, so that $14s=8{\cdot}78$ and probably inadmissible.

(15) is $-9\delta_1$ on (14) and is $(-7\delta_1)S_1$.

(20) is $79{\cdot}33=\nu_1+\nu_2-{\cdot}65$ ahead of (15), *i. e.* S_1 changed to S_3 and a $+\delta_1$ displacement. It is $(-6\delta_1)S_3$.

(16) shows no mutual oun shifts, as it should not, since it is $S_1'''(2)$.

There are few lines in the D region. (1) is another of Rowland's lines seen in the sun, and observed by no one else. (2) is $S_2'''(3)$. It shows a just possible oun multiple shift to (4), where $11{\cdot}22=8\times1{\cdot}3911+{\cdot}09$, but doubtful. It would be $(-8\delta_1)S_2'''(3)$. (6) has been allocated above to $(2\delta_1)D_1{}^n$. (3·5) show the σ_1 separation of this series, viz.:— $14{\cdot}15=\sigma_1-{\cdot}07$. As (3) is 43·65 behind (6) it suggests a ν link or a $40\delta_1$ displacement on (6) which gives a shift= 43·86. But in either case a simultaneous displacement in ϕ is required, viz.:—*a*. $(2\delta_1)$ D $(10\delta_1)$ or $(42\delta_1)$ D $(-6\delta_1)$, *if* the observed lines have no error. It is denoted in the list as *a*. $(2\delta_1)$ D_1 ?, making (5) therefore=*a*. $(2\delta_1)$ D_2 ? Then (4), 2·22 ahead, means the annulment of the $2\delta_1$ displacement and is *a*. $D_1{}^n$?. Further (7)—an E. H. line — is 58·99 ahead of (6) and $d+\sigma_1=58{\cdot}59$. An error $d\lambda$ 2·04 as between E. H. and Fritsch is quite possible. This would make $(7)=(2\delta_1)D_2{}^n\,.\,d$. (8) would be 10·93 ahead of the corrected (7) and would be accounted for by σ_2 and the annulment of the $2\delta_1$ displacement, viz.:— $8\ 70+2{\cdot}19=10{\cdot}89$. Thus $(8)=D_3{}^n\,.\,d$. For our present purpose the important point

is that we here find the σ_1, σ_2 separations appearing in possible allocations on the independent and not on the singlet hypothesis for (3) is too far ahead of (1)—given below as a possible D′ line—to bring them within the singlet ambit.

On the S′ hypothesis, judging from the case of $m=4$, we are to expect a line close to and somewhat larger than the calculated value. We find this at (6) or (7) with a ν_1 forward and a D′ line at 1 in list D about C ahead. This last line is another of Rowland's sun lines, and observed by no one else. The separations from (6, 7)=10972·40, 1·61 are C+4·65, +3·86, while (6, 7) are decisively not mutual limit collaterals. The excess 4·65 has no obvious relation to oun shifts, but $3{\cdot}86 = {\cdot}62 + 3\times 1{\cdot}08$, or exactly one oun displacement on S′ and three on D′. But the exactness again must be a pure coincidence since the lines are measured by different observers. Taking this indication however, (7) in S is $(-\delta_1)S_1'$ and (1) in D is $(3\delta_1)D'$ or $S_1'(5)=20593{\cdot}70$, $D_1'(5)=31561{\cdot}45$. The excess 4·30 over the calculated is larger than we should expect, compared with ·46 for $m=4$. (9) in S is 43·73 ahead of (7). This has no reference to a displaced S_2' line unless the S_2 has displacement also in the ϕ term. Numerically it is 44·36—·63 or the d link with $+\delta_1$ on limit, *i. e.* is $S_1'(5)\,.\,d$. without any displacements. But if so there is no allied S_2' seen. (7)—(5)=8·62=14s—·06 or a 14 oun displacement on S′ basis and probably not on S^n basis. Thus (5)=$(13\delta_1)S_1'$. There is definitely no connexion with (8). There is nothing to be gained by following up the connexions further. Comparing the two theories we find

$$\begin{array}{l|l} (2\delta_1)S_1^n \quad (2\delta_1)D_1^n & (-\delta_1)S_1' \qquad\qquad (3\delta_1)D_1'. \\ \quad (\delta)S_2^n\, a\,.\,(2\delta_1)D_2^n & \quad (?)S_2'(?)=S_1'\,.\,d \\ (-6\delta_1)S_3^n\,(2\delta_1)D_2^n\,.\,d\,D_3^n\,.\,d & \end{array}$$

with a doubt as to the real existence of the D′ line.

Although the discussion of the "singlet" data affords good illustrations of the displacement effect, it unfortunately does not give any clear and certain discrimination between the two hypotheses as to the nature of these series, although perhaps on the whole it favours that of independent origin. The reason for this is that the links have the same value on either hypothesis, and that the two limits, 24189, 24405, are so close that the shifts per oun on them are very nearly the same for the same wave-number. Differences in multiples of these shifts therefore only become greater than possible observation errors when these multiples are very large.

But we have met with one possible criterion which may be found to weigh heavily against the singlet hypothesis. This is the allocation of lines for $S'(4)$ and $D'(5)$ which have been observed by Rowland when identifying the origin of very faint lines seen by him in the sun, and seen by no other observer. If the existence of these lines as due to Mn is established we get a very strong support for the singlet theory, especially as a complete triplet would then be found for $S'(4)$. If after a special search no such line can be found, the argument against this theory would become very strong.

The oun relations, (see III.) while favouring the singlet hypothesis where the two multiplet terms ϕ_1, ϕ_2 are concerned, are decisively against it, in connexion with the triplet separation sum, 79·98, *if* these new terms are subject to the same rules as those obeyed by the hitherto known terms. It would seem that the question of the nature of these new series must remain open for the present.

XXXV. *Observations on the Note of Dr. L. Silberstein: Determination of the Curvature Invariant of Space-Time* (Phil. Mag. xlvii. 1924, pp. 907–917). *By* H. Weyl, *Professor a. d. Eidg. Techn. Hochschule, Zuerich* *.

1. Dr. Silberstein maintains (footnote, p. 909) that "tan" ought to stand for "sin" in my formula for the displacement to the red τ, for this is the result furnished by his own formula (5, p. 912) for $\gamma=1$. But in my case r signifies the distance of the star measured in the static space of the observer at the moment of observation. For Dr. Silberstein, on the contrary, r signifies a very artificial (in some instances complex-imaginary) quantity—namely, the distance of the star from the observer at the moment of observation, but in the static space of the star.

2. I have by no means "more or less disguised as a necessary feature of de Sitter's world" the assumption regarding the world-lines of stars. On the contrary, going further than de Sitter and Eddington, I strongly emphasized the necessity for *adding* an assumption regarding the "undisturbed state" of stars, if anything in the theoretical line regarding the displacement to red is to be formulated. The hypothesis also which I have pursued arithmetically is not "perfectly gratuitous," but simply means that the stars of

* Communicated by the Author.

† *Raum Zeit Materie*, 5. Auflage, Berlin, 1923, p. 323; *Physikalische Zeitschrift*, xxiv. p. 230 (1923).

the system are able to act upon one another from eternity. Another hypothesis has been followed by Mr. K. Lanczos *, but mine has the great advantage of not introducing a singular initial moment, of conserving the homogeneousness of time. (Moreover, it is the only one which satisfies this requirement.) However, the cosmology arrived at in this way remains also for me—that is self-understood—an hypothesis, even a rather daring but nevertheless reasonable hypothesis.

3. Curiously enough, Dr. Silberstein at the end of his articles uses exactly the same assumption as a basis, the only difference being that he adds to my group of world-lines, which diverges into the future, that which results from it through the interchange of past and future (double sign). That, I must confess, appears quite abstruse to me. If (according to the opinion of van Maanen and Shapley) the conception which has been developed by Charlier, Lundmark and others is erroneous—the conception, namely, that the spiral nebulæ are extra-galactic and in consequence a good deal further off than the other heavenly bodies, including the globular clusters,—then, of course, the cosmological interpretation of that pronounced displacement to the red which the spectrum-lines of the greater majority of them show becomes impossible.

Zuerich, 15 June, 1924.

XXXVI. *The Electrical Conductivity and certain other Properties of Metals and Alloys on the Basis of Bohr's Theory.* *By* Kristian Højendahl, *Danish Government Ramsay Memorial Fellow* †.

Introduction.

METALS and alloys form an outstanding group of bodies possessing certain characteristic properties. Theoretical explanations of these properties have already been put forward by various authors.

In this paper the attempt is made to show to what extent such properties can be accounted for on the basis of the rotation of the elliptic orbit of the valency electron, which, according to Bohr ('Nature,' vol. cxii. p. 29, 1823), is much more pronounced for the case of metals than for hydrogen. The reason for this rotation is that the field-force is stronger

* *Zeitschrift für Physik*, xvii. pp. 168–189 (1923).

† Communicated by Prof. W. C. M. Lewis.

inside the inner electron shells than it is outside. In passing from lithium to carbon in the periodic system, the difference between the inside and the outside of the K shell diminishes; and it can therefore be understood why the rotation of the elliptic orbit can be overcome in the case of carbon atoms chemically bound, whilst this is not the case for lithium.

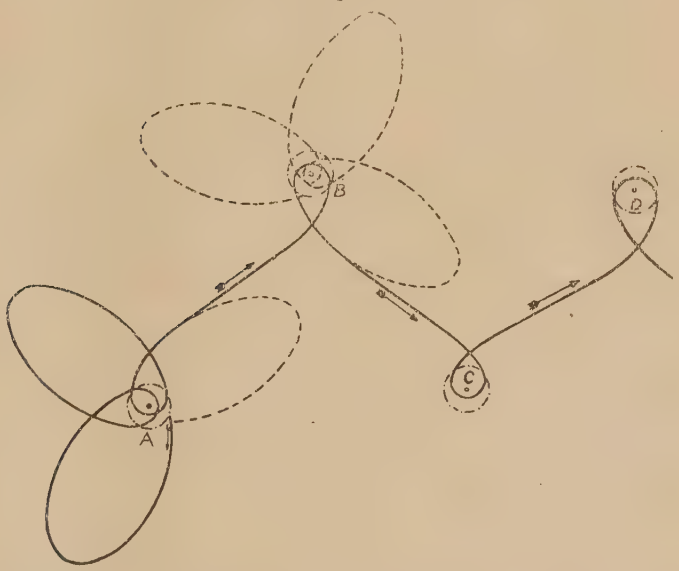
The "shared" electrons constituting a typical organic (covalent) bond are assumed to move in shared orbits similar to the figure of eight proposed by Sidgwick (Trans. Faraday Soc. vol. xix. pt. 2, p. 469, 1923). The shape of a loop in a figure of eight is very similar to that of the inner loop in an elliptic orbit with a small rotation. This analogy might also be expected for the following reason. Near to one atom the influence of other atoms on the orbit of an electron must be small. The electron, therefore, will move very nearly in the same path as it would if the other atoms had been absent—that is, in the free atoms. This agrees with the view expressed by R. H. Fowler (Trans. Faraday Soc. vol. xix. p. 459, 1923), who assumes that the loop of a shared orbit in a (compound) molecule may replace and represent the inner part of an unshared orbit in an isolated atom.

The General Structure of a Metal.

The manner in which electrons possessing considerable orbital rotation can form covalent bonds between pairs of atoms may be illustrated as follows. Let us take 2 atoms of vaporized lithium (A and B in fig. 1). Only the orbit of the valency-electron originally belonging to one of the atoms, namely A, is considered. It describes a rosette round A, as shown in the figure. When an outer loop comes close to B, it may happen that the attraction from B on the electron will be so strong that it will balance that from A, and the electron will therefore move in a straight line towards B. Near B the field of B is the dominating one. The electron therefore moves round B in nearly the same way as does an electron in a free atom—*i. e.*, in the dotted rosette. It will be realized that the electron, when moving in the rosette, will not be expelled into the sphere of attraction of A before it has passed the whole way round in the rosette. Only for the time-interval during which the electron is passing between the atoms can these be considered as bound together with a covalent bond. This happens only at intervals, and consequently the bond in this case is not a stable one, and metallic vapours are practically monatomic.

If, however, the liquid or solid state is considered, there will be a third atom C and a fourth atom D relatively close to A and B, as shown in the diagram. If this is the case, the electron, when expelled from B, may be caught by C traversing a *rosette*-shaped path around it, and then in turn may be captured in a similar manner by D, and so on in a zigzag path throughout the metal.

Fig. 1.



For the case of a crystalline metal the atoms are arranged in a space-lattice. The zigzag paths of the electron, therefore, will be very regular and placed in a number of equivalent directions. The atoms are thus knitted together in many directions by electronic orbits. Electrons follow rapidly in the same path at definite intervals. Every time an electron passes over between two atoms, these may be considered as bound together with a covalent bond. When a crystal of a metal is disintegrated, such bonds must be broken. Similar bonds are not broken by the disintegration of other crystals. Thus the bonds, which are broken in the case of a crystal consisting of organic molecules, are those weak attractions, due to polarity only, which join the molecules together. Such molecular attractions are not due to covalency, as envisaged above. The bonds broken in the case of a salt are the electrostatic

attractions between the ions. In non-metals, only in a few cases such as the diamond are actual covalent bonds broken. It should be emphasized that the passage of the "covalent" electrons here considered, although involving translations from place to place, is wholly different from the old and now-discarded theory of freely-moving electrons. The motion here considered is a quantized one.

Another comparison between crystalline substances is suggestive—namely, that the heat-conductivity is high in all cases where electrons pass over in quantized paths between the atoms as in the case of the diamond and the metals; whilst for the cases of salts and organic crystals, where such transitions do not take place, the heat-conductivity is low. It must therefore be assumed that the energy of the electrons varies (very slightly) with temperature. The valency-electrons, however, do not possess measurable heat-capacity, since their characteristic quantum energy is supposed to be very high. The marked conductivity is due in part to the *rapidity* of motion of the valency electrons.

The quantum energy of the valency-electron arises because the zigzag path of the electron represents the path of an oscillator, which moves from one atom to its neighbour for one vibration. This means that the shape and dimensions of the path, and the velocity, energy, and frequency of the electron, approximate (closely) to definite values. Thus also the dimensions of the crystal-lattice are fixed. The crystalline form which the metal takes up is determined mainly by the angle of rotation (ϕ in fig. 2). The definite state, however, only appears at the absolute zero. At higher temperatures the vibrations of the atoms will be superimposed on the motion of the electrons, and cause slight changes in the total energy of the electron and in the dimensions of the crystal. The change in the total energy of the electron is the ultimate cause of heat-conduction.

The Electrical Conductivity of Pure Metals.

It is evident that the system outlined above will be an excellent conductor for electricity. In its consequences it is similar to a theory of Wien (*Berl. Ber.* vol. vii. p. 184, 1913); in fact, it gives a model for Wien's theory. Wien's treatment is based on Drude's equation:

$$\sigma = \frac{1}{2mu} e^2 \mathrm{NL}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where σ is the specific conductivity, u the *mean velocity* of

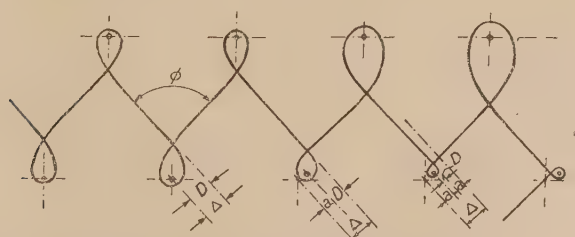
the electron and e its charge, L the mean free path, and N the number of free electrons in 1 c.c.

Wien assumes that u and N are constant ; L is the only temperature variable that remains. Furthermore, Wien assumes that the path of an electron is changed abruptly by *vibrating* atoms only, and that the probability of an abrupt change is proportional to the square of the amplitude of the atom. Introducing Debye's theory, he arrives at the following equation for the specific resistance :

$$w_T = C\frac{kT\nu_m}{h}\left(1-\tfrac{1}{4}\rho_m+\tfrac{1}{36}\rho_m^2-\tfrac{1}{3600}\rho_m^4\right), \quad . \quad . \quad (2)$$

where $\rho_m = \frac{h\nu_m}{kT}$ and ν_m is the maximum frequency. The equation is in good agreement with experiment. The resistance vanishes before the absolute zero is reached, and the temperature-coefficient for normal temperatures becomes somewhat larger than 1/273. A basis for Wien's assumptions is found in the present model. As has already been shown, the velocity of an electron is constant. Also, as shown in fig. 2, the actual zigzag path pursued constitutes, owing to its persistence, an effective linear motion in one direction—*i. e.*, parallel to a row of atoms. This would go on indefinitely, if all the atoms were at rest and of the same kind, and thus give rise to the superconductivity at absolute zero. If, however, one of the atoms is displaced, the path will be disturbed in the way shown in fig. 2, and if the displacement is large enough, the path will be abruptly changed in direction by a definite characteristic angle in the crystal. Even if the effect is not due to a single atom, the disturbances of the path caused by several displaced atoms will sum up and finally cause an abrupt change in direction,

Fig. 2.



as shown in fig. 2. The new effective direction pursued by the electron will be parallel to another row of atoms in the crystal. The mean length of the "unbroken" path between

two such abrupt changes in direction is considered as being analogous to the mean-free-path in Drude's theory. A single "unbroken" path obviously consists in general of a certain number of zigzag "vibrating" movements. A single "vibration" is not to be taken as the analogue of the mean-free-path of the older view.

The degree of disturbance of the quantum path of the electron may be represented by the change in the distance D (fig. 2) between the nucleus of an atom and the tangent to the point of inflexion in the preceding branch of the electron's quantum path. The normal value of this distance is Δ. As shown in fig. 2, the thermal displacement a of the atom is subtracted or added directly to Δ to give the value of D at the first displaced atom. The displacement a of one atom will cause a corresponding disturbance of the electron motion at all the succeeding atoms. Whether these disturbances are larger or smaller than a depends on the nature of the field-force of the atoms. It is assumed that the disturbance of the electron caused by a displacement a of one atom will appear with the same magnitude at the succeeding atoms. When the total disturbance becomes larger than Δ, *i. e.* $D=0$, the electron will be expelled to the "wrong" side of the last atom in the sequence, and the path will be abruptly changed in direction. The displacements of the atoms are not all to the same side, but distributed according to probability laws. The total disturbance therefore follows the rule for summation of experimental errors. Consequently, the number of atoms n which on the average are necessary for obtaining a total disturbance Δ of the electronic path is given by the equation :

$$\Delta = \bar{a}\sqrt{n}$$

$$\text{or} \quad \frac{1}{n} = \frac{\bar{a}^2}{\Delta^2}, \qquad (3)$$

where $\bar{a}$ is the mean amplitude (displacement) of the atoms.

The above equation (3) shows, in agreement with Wien's assumption, that $\frac{1}{n}$, the probability for "break" or abrupt change of the path of an electron, is proportional to the square of the amplitude of the atom.

It follows from this that the probability of a "break" is (approximately) proportional to the heat-energy of the atom; this means in turn that the magnitude of the resistance is proportional to the heat-content. At sufficiently high

temperature the heat-content becomes proportional to the absolute temperature. Hence also the resistance becomes proportional to the absolute temperature.

The Electrical Conductivity of Alloys.

A more marked disturbance, *i. e.* a more frequently occurring effect, may appear in the path of an electron when an atom in the crystal is replaced by an atom of another kind. The foreign atom necessarily alters the characteristic angle ϕ, with the result that the effective direction of the path of the electron is abruptly changed, generally at the foreign atom.

The resistance R_0, which arises in this manner, depends on the heterogeneity introduced; the alloy-resistance R_0 persists at the absolute zero, and is practically a constant for all temperatures. In addition to the above effect, the heat-vibrations also will cause "breaks" (abrupt changes in direction) in the normal way, and give rise to a certain resistance R_T, which depends on temperature in the known manner. From what has been said already, it follows that at 0° C. the temperature-coefficient with respect to R_T alone is

$$\frac{1}{R_T} \cdot \frac{dR}{dT} = \text{circa } \frac{1}{273}.$$

With respect to the total resistance of an alloy, the temperature-coefficient becomes

$$\frac{1}{R_0 + R_T} \cdot \frac{dR}{dT} = \frac{1}{273} \cdot \frac{R_T}{R_0 + R_T}. \quad . \quad . \quad . \quad . \quad (4)$$

For ordinary alloy-compositions, R_0 is generally much larger than R_T; hence it will be seen that the temperature-coefficient of alloys (mixed crystals) is small. If R_T is the linear mean of the resistances of the components, the above expression is identical with the empirical expression given by Matthiessen, as cited by Guertler (*Jahrb. Radio-Elektr.* v. p. 17, 1908).

If it be assumed that the electron-path is always "broken" (abruptly changed in direction) at a foreign atom, an expression for the relation between the composition of the alloy and the specific alloy resistance R_0 may be obtained in the following manner.

Let us consider the probability p that the path of any electron shall be "broken" or not "broken" at any atom

in a mixture of a atoms of a metal A and b atoms of another metal B. The condition that a "break" shall occur is that the preceding atom shall be of another kind. The sequences B–$\overset{\times}{\text{A}}$–B and A–$\overset{\times}{\text{B}}$–A will give "breaks" at the crossed atoms, and therefore not at the last ones. B–B–$\overset{\times}{\text{A}}$ and A–A–$\overset{\times}{\text{B}}$ will give a "break" on the last atom. The probabilities that the atom considered shall be the last one in a sequence of the latter type are

$$\frac{ab^2}{(a+b)^3} \text{ and } \frac{a^2b}{(a+b)^3} \text{ respectively;}$$

$$\text{total probability} = \frac{ab}{(a+b)^2}.$$

These are the most predominant, but not the only combinations, which lead to a "break" on the last atom; others are (BB$\overset{\times}{\text{A}}B\overset{\times}{\text{A}}$ and AA$\overset{\times}{\text{B}}A\overset{\times}{\text{B}}$) and (BB$\overset{\times}{\text{A}}B\overset{\times}{\text{A}}B\overset{\times}{\text{A}}$ and AA$\overset{\times}{\text{B}}A\overset{\times}{\text{B}}A\overset{\times}{\text{B}}$) etc., with the probabilities

$$\frac{a^2b^3}{(a+b)^5}+\frac{a^3b^2}{(a+b)^5}=\frac{a^2b^2}{(a+b)^4},$$

$$\frac{a^3b^4}{(a+b)^7}+\frac{a^4b^3}{(a+b)^7}=\frac{a^3b^3}{(a+b)^6}.$$

The total probability p that the path shall be "broken" at any atom is given by the sum of the progression:

$$p=\frac{ab}{(a+b)^2}+\left[\frac{ab}{(a+b)^2}\right]^2+\left[\frac{ab}{(a+b)^2}\right]^3+\ldots=\frac{\dfrac{ab}{(a+b)^2}}{1-\dfrac{ab}{(a+b)^2}}.$$

The average distance L (in lattice spacings) between two consecutive "breaks" (or abrupt changes in direction)—which distance, on the old view, would be the mean-free-path of the electron—is given by the inverse of the expression for p. That is,

$$\mathrm{L}=\frac{1-\dfrac{ab}{(a+b)^2}}{\dfrac{ab}{(a+b)^2}}. \quad \ldots\ldots\ldots \quad (5)$$

According to Drude's equation (equation 1),

$$R_0 = \frac{2mu}{e^2N} \cdot \frac{1}{L} \cdot \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Inserting the expression for L, denoting the atomic fraction $\frac{a}{a+b}$ by c_1 and $\frac{b}{a+b}$ by c_2, and putting $\frac{2mu}{e^2N}$ equal to C, the following expression is derived :

$$R_0 = C \cdot \frac{c_1c_2}{1-c_1c_2} \cdot \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

C is only a constant in so far as the velocity u is the same for the two metals.

The above relation is very similar to an empirical relation given by Guertler (*Jahrb. Radio-Elektr.* v. p. 17, 1908), namely

$$W_2 = CK(100-K),$$

where $W_2 = R_0$; K is volume-percentage, and C a constant. He obtains a good agreement for the alloy Ag–Au (where atomic fractions and volume-percentage are proportional). In the following Table I., equation (7) has been tested on the experimental values for the alloys Cu–Ni given by Feusner (*Landolt-Börnstein*, 5th ed. p. 1054). In this case also, volume-fractions are equal to atomic-fractions. The temperature-resistance R_T is taken as the linear mean of those of the components, employing the familiar "mixture law" formula.

TABLE I.

Volume per cent. nickel.	Atomic fraction.	Total resistance.	R_T.	R_0.	$C=\frac{2mu}{e^2N}$.
0·0	0·000	16·2	16·2	0·0	
10·5	0·105	149·0	27·4	121·6	1170
20·8	0·208	266·4	38·3	228·1	1156
25·0	0·250	316·2	42·7	269·5	1163
31·0	0·310	392·2	48·2	344·0	1260
41·0	0·410	488·0	59·7	428·3	1340
51·2	0·512	540·0	70·6	459·4	1380
63·0	0·630	500 0	83·0	417·0	1375
92·8	0·928	185·0	115·0	70·0	980
96·6	0·966	165·0	119·5	46·0	1540
100·0	1·000	122·5	122·5	0·00	

The table shows as good a constancy for C as can be expected in view of the variation in u.

If actually the path of every electron is "broken" every time it arrives at a foreign atom, the rise in resistance caused by introduction of a small amount of another metal (B) may lead to a determination of the distance between two

consecutive abrupt changes in the effective direction of the path or, as it also may be termed, the mean length of the "unbroken" path of the electron in the pure metal A. For this case (c_1 small) the above equation gives

$$R_0 = \frac{2mu}{e^2N} \cdot \frac{c_1 \times 1}{1}.$$

The total resistance is this plus the temperature-resistance R_T, which is the same as that for the pure metal A. According to equation (1),

$$R_T = \frac{2mu}{e^2N} \cdot \frac{1}{L}.$$

The velocity u is the same for the pure and the impure metal, and consequently for the metal A:

$$L = \frac{1}{c_1} \cdot \frac{R_0}{R_T} \text{ lattice-spacings.} \quad . \quad . \quad . \quad (8)$$

Now consider another alloy of the metal A—namely A mixed with C. If an atom of C "breaks" the path of an electron at every collision therewith, the mean length of the "unbroken" path calculated on the basis of the A–C alloy should give the same result as that calculated on the basis of the A–B alloy. This actually seems to be the case, as shown below in Table II. The experimental data are mainly taken from a diagram in Guertler's paper (*l. c.*).

TABLE II.

Resistance of iron with 2 weight-percent of other metals. Mean length of "unbroken" path in iron.

	Atomic fraction.	Total resistance.	Resistance of iron.	R_0.	L calculated from Guertler & Matthiessen's data.	L calculated from other investigators' data.
W	0·006	119	76	43	72·0	
Au.....	0·0057	139	...	63	110·0	
Ni	0·019	161	...	85	44·7	
Cr	0·0214	192	...	116	54·2	
Mn ...	0·0203	210	...	134	66·0	50
Si	0·0394	335	...	259	66·0	63 : 67
Al.....	0·0413	370	...	294	71·3	58
C	0·0930	660	...	584	63·0	
Cu.....	...	...	...	...	...	42

Gold seems to be the only exception in so far as the value for it is definitely outside the experimental error, which is very large. The mean length of "unbroken" path for the valency-electron in iron is about 60 lattice-spacings—*i. e.*, about $1{\cdot}7 \times 10^{-6}$ cm.

In the same manner the mean length of the "unbroken" path of (probably impure) platinum is found to be about 8 lattice-spacings.

For solid mercury L is about 9, based on mercury-sodium alloy. If this is the correct value, the mean length of the "unbroken" path in liquid mercury will only be about 2 lattice-spacings if the same proportionality holds for the liquid as for the solid state.

When the mean length of the unbroken path has been determined in this manner, the velocity of the electron may be determined by help of equation (6)—viz.,

$$R = \frac{2mu}{e^2 N} \cdot \frac{1}{L}.$$

Inserting the value for iron, a velocity of the order $4{\cdot}3 \times 10^8$ is obtained. As might be expected, it is of the same order as the velocity of an electron in a hydrogen atom.

Taking the lattice-spacing as $2{\cdot}83 \times 10^{-8}$, the vibration-frequency of the electron considered is $1{\cdot}5 \times 10^{16}$—*i. e.*, a quantity so large that any energy term dependent upon it would be negligible in specific-heat measurements.

Summary.

1. On the basis of the Bohr atom, with special reference to the rotation of the orbit, the attempt has been made to envisage the formation of a *di*-atomic compound in a metallic vapour by the sharing of electron orbits. A permanent diatomic compound cannot be formed, and in the state of vapour the metal must be monatomic. It is, however, possible to form an infinite-atomic compound (the metallic state). In this an electron does not move inside a limited space ; but it moves in a quantized zigzag path throughout the metal.

2. The shape of this path, the distances between the atoms, and the energy and velocity of the electron will be determined by quantum rules. Hence they will be only slightly dependent on temperature.

3. In a perfect crystal at the absolute zero the paths will be regular, of the same length as the crystal, and placed in a number of equivalent directions parallel to rows of atoms. The direction of the path may be abruptly changed, *i. e.* "broken," by (*a*) the heat-vibration of the atoms, by (*b*) irregularities in the crystal, and (*c*) by introduction of atoms of another kind.

4. The "unbroken" path is the analogue of the free-path in Drude's classical theory. The specific electrical conductivity, then, is proportional to the mean length of the "unbroken" path.

5. The present model provides a basis for the assumptions underlying the theoretical treatment of Wien on the relation between electrical conductivity and temperature.

6. It indicates why alloys have a high resistance and a low temperature-coefficient. A theoretical expression for the relation between resistance and composition of a perfect mixed crystal is worked out in fair agreement with experiment.

7. The rise in resistance caused by introducing 1 atom of a number of metals into 100 atoms of a pure metal (A) is nearly constant for the same pure metal. This leads to a determination of the mean length of the "unbroken" path in metal A expressed in lattice-spacings

8. On this basis the velocity of the covalent electrons in iron has been calculated, using Drude's equation. The calculated velocity is of the right order of magnitude.

The author desires to express his thanks to the Ramsay Memorial Fellowship Trust for a grant.

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XXXVII. *The Band Spectrum of Mercury and the Dissociation of Hydrogen Molecules by Excited Mercury Atoms.* *By* K. T. Compton, *Ph.D., D.Sc., Professor of Physics, and* Louis A. Turner, *M.A., Ph.D., Charlotte Elizabeth Procter Fellow in Physics, Princeton University* *.

IT has long been known that an electric discharge of low intensity in mercury vapour causes the appearance of a band spectrum. In addition to the green and ultra-violet unresolved bands, prominent in the fluorescent spectrum and ascribed to Hg_2 molecules formed in the presence of excited atoms †, there have been found several bands with resolvable structure ‡. The earlier workers found that these bands were enhanced in intensity when a stream of vapour was maintained in the discharge-tube by evaporating mercury at one end and condensing it at the other. The heads of the most intense bands are of wave-lengths 4219, 4017, and 3728. They shade off toward the short wave-length side, and are made up of comparatively easily resolvable lines of which the wave-lengths were measured by Liese §. Bands of similar structure have also been found in the spectra of zinc and cadmium. These band spectra have been analyzed by Hulthen ‖, who came to the conclusion that the emitters of these spectra must be molecules composed of heavy metal atoms and atoms of an element of low atomic weight, since the wide spacing of the lines

* Communicated by the Authors.

† Franck and Grotrian, *Zeits. f. Phys.* iv. p. 89 (1921).

‡ Kayser, *Handbuch der Spektroscopie*, vol. v.

§ E. Liese, *Zeit. wiss. Phot.* xi. p. 349 (1912).

‖ Erik Hulthen, *Zeit. für Physik*, xi. p. 291 (1922).

indicates a small moment of inertia of the molecules. He suggested a nitrogen compound as a possibility, owing to certain simultaneous variations of intensity of these bands and those of nitrogen, when the conditions of excitation were varied. Kratzer * analyzed these spectra also, revised Hulthen's arrangement somewhat, and came to the conclusion that the emitters must be molecules of a hydride rather than of a nitride, since their moment of inertia is less than that of a nitrogen molecule. Mulliken † has recently pointed out that these bands show no evidence of separations due to the different isotopes of the metals, and has shown that this fact favours the theory that the bands are emitted by hydride molecules.

We have obtained experimental results of a different kind, which confirm this theory that the band spectrum of mercury is emitted by molecules of a mercury hydride. We have taken photographs of the spectrum of the light emitted by the positive column of a Geissler discharge in a tube with a tungsten filament cathode, containing mercury vapour at a pressure of 0·3 mm. and hydrogen at different pressures from 0·16 mm. down, with 80 volts applied to the anode. The band spectrum is quite strong in comparison with some of the lines of medium intensity in the mercury spectrum at the higher pressures of hydrogen, and is almost entirely gone when the hydrogen is pumped out by a diffusion pump. Its strength is roughly proportional to the hydrogen pressure. This we consider to be a good indication that the bands are due to the hydride of mercury. This experiment is somewhat of a confirmation of the quantum theory of band spectra, since Kratzer's calculation of the moment of inertia of the molecule was based on that theory. This experimental arrangement gives a good source of the light of this band spectrum, which should be of use to anyone with the proper spectroscopic equipment who might wish to extend our knowledge of this spectrum by a study of the structure of some of the weaker bands. Apparently the evaporation and condensation of the mercury in the earlier experiments caused the production of hydrogen in the tube which would otherwise have remained dissolved in the liquid mercury.

The question arises as to whether this spectrum is emitted following the excitation of mercury hydride molecules existing in the tube, or whether these molecules form by the reaction of hydrogen with excited mercury atoms. We believe that the latter process is the one which occurs. W. H. McCurdy has made an extensive study of the discharge in mercury vapour in a tube of this sort. He found that the positive

* A. Kratzer, *Ann. der Physik*, lxxi. pp. 9–12, 72 (1923).
† R. S. Mulliken, 'Nature,' cxiii. p. 489 (April 5, 1924).

column was uniform when the mercury vapour was pure, but became striated when impurities were present. He introduced hydrogen in order to produce the striations. His measurements of the density of the electrons, their mean velocity, their velocity distribution, and the potential gradient in the striated discharge, which are to be published later, show that the bright parts of the striations are the regions where many inelastic impacts occur, resulting in the formation of mercury atoms in the $2p_1$, $2p_2$, and $2p_3$ states. Consideration of the mobilities of electrons of different velocities and of space-charge effects leads one to expect a striated discharge, provided that the excited atoms in the $2p$ state do not diffuse far away from their place of formation, thus offering the possibility of inelastic collisions with electrons of almost any low velocity at any place in the tube. The function of the hydrogen is apparently the prevention of this diffusion of metastable excited mercury atoms throughout the tube by collisions of the second kind in which the energy of the excited atom is used up in dissociating the hydrogen molecule, as in the experiments of Cario and Franck *. When the hydrogen is pumped out, the excited atoms diffuse throughout the tube and the striations disappear. According to this theory, the bright parts of the striations should be regions of high concentration of mercury atoms in the $2p$ excited states. We have found that the subordinate series lines of mercury 5461, 4358, and 4047, $2p_{1,2,3}-2s$, are much more strongly absorbed in these regions than in the dark spaces between striations. This theory and these experiments will be discussed fully in another paper. We also find that the band spectrum of mercury hydride is emitted from the regions of high concentration of excited mercury atoms. This would not be the case if the emission of the spectrum resulted from the excitation of already existing hydride molecules, and did not depend upon the presence of excited mercury atoms.

Cario and Franck suggested as a possible explanation for their experimental results on the clean-up of hydrogen molecules by excited mercury atoms that the excited atom gave up its energy to dissociate the hydrogen molecule into the two atoms, the excess energy appearing as kinetic energy of the three resulting atoms. This explanation meets with difficulties, however, if we consider thermal equilibrium in a region containing hydrogen and mercury. Such considerations are analogous to those which originally led Klein and Rosseland † to the idea of collisions of the second kind. In

* G. Cario and J. Franck, *Zeit. für Phys.* xi. p. 161 (1922).

† O. Klein and S. Rosseland, *Zeit. für Physik*, iv. p. 46 (1921).

order to maintain the equilibrium, this dissociation of hydrogen would have to be counterbalanced by the reverse process, which would be the simultaneous encounter of two hydrogen atoms and a mercury atom, resulting in the formation of a hydrogen molecule and an excited mercury atom. The colliding atoms would need to have enough kinetic energy so that its sum with the energy of combination of the hydrogen atoms would be sufficient for excitation of the mercury atom. This is a most improbable happening. The present experiments suggest an explanation which presents fewer difficulties. It is that the excited mercury atom reacts with the hydrogen molecule to form a hydrogen atom and an excited molecule of mercury hydride. This excited molecule radiates the band spectrum, and then may dissociate into a normal mercury atom and a hydrogen atom. This explanation accounts for the experiments of Cario and Franck and our experiments on the band spectrum, and offers fewer difficulties in the consideration of the thermal equilibrium. It should be pointed out that this possible different explanation of the process makes no difference in the calculation of the average life of the mercury atom in the $2p_2$ state made by one of us *, upon the basis of the measurements of Cario and Franck.

Summary.

1. The band spectrum of mercury, the heads of the three strongest bands of which are of wave-lengths 4219, 4017, and 3728, is developed strongly in a Geissler discharge in a tube containing a mixture of mercury and hydrogen, but disappears when the hydrogen is pumped out. This supports Kratzer's conclusion, based upon a study of the structure of the bands from the point of view of the quantum theory, that the emitters of the bands are molecules of a hydride of mercury.

2. The bands appear in the regions of the striated discharge where the concentration of excited mercury atoms in the $2p$ states is greatest. This fact indicates that the presence of these excited atoms is necessary for the production of the bands.

3. It is suggested that an excited mercury atom reacts with a hydrogen molecule to form an excited hydride molecule and a hydrogen atom rather than to dissociate the hydrogen into two atoms immediately, by a collision of the second kind.

Note added with the proof.—An attempt was made to excite these bands optically by absorption of resonance 2536 radiation in a mercury-hydrogen mixture, but without success.

* Louis A. Turner, Phys. Rev. xxiii. p. 464 (1924).

XXXVIII. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from vol. xlvii. p. 784.]

March 12th, 1924.—Prof. W. W. Watts, Sc.D., F.R.S., Vice-President, in the Chair.

THE following communication was read :—

'The Old Red Sandstone of the Cardiff District.' By Albert Heard, M.Sc., F.G.S., and Richard Davies, M.Sc.

This paper gives an account of an exhaustive petrological investigation of the Old Red Sandstone of the Cardiff District. During the course of the work, a new fish-band was discovered in the Red Marl Group. This Coed-y-Coedcae Fish-Bed contains innumerable fragments of *Cephalaspis* and *Pteraspis*, together with *Pachytheca* and obscure plant-remains.

The petrological investigation revealed a rich assemblage of pebbles and minerals. Among the pebbles, vein-quartz and opalescent quartz are the most abundant, with numerous acicular, irregular, and especially regular inclusions. Evidence of intense mechanical deformation is generally exhibited. Cherts, jaspers, and pebbles of quartz-gneisses, mica-schists, sandstones, and quartzites are abundant. Pebble-beds, with sandstone-pebbles not assignable to any Lower Palæozoic sediments, are of common occurrence in the Red Marl Group. The finer constituents include quartz-grains similar to larger quartz-pebbles, abundant fresh microcline and oligoclase, and many large flakes of white mica and chlorite; fresh biotite occurs in the cornstones.

The 'heavy' minerals include ilmenite and leucoxene, pyrites, garnet, tourmaline, a large proportion of coloured to colourless zircons, rutile, apatite, and a little magnetite.

Three definite mineralogical zones are established, corresponding roughly with the stratigraphical groups.

The cornstones have been investigated, and partial chemical analyses made. A physico-chemical origin is suggested.

The sediments are compared with the Torridonian and Millstone Grit of Yorkshire, and it is concluded that the Old Red Sandstone of the Cardiff district represents estuarine and deltaic deposits derived mainly from a pre-Cambrian massif on the north-west.

The Silurian rocks of the Cardiff district have been investigated, and have proved to be entirely different and distinct from the Old Red Sandstone. No pebbles from the Silurian have been observed in the lowest Old Red Sandstone beds. It is concluded that the definite petrological break represents a non-sequence. The hypothesis of the 'Welsh Lake' is considered to be untenable.

A probable connexion with the Devonian of North Devon is suggested.